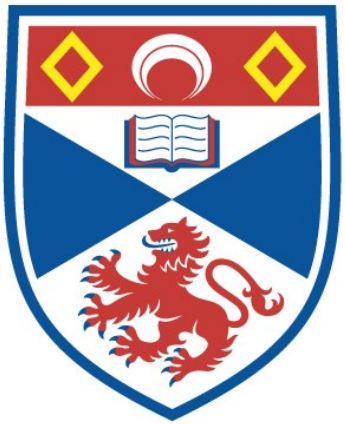
SOME REACTIONS OF ALKYL RADICALS

Derek G. Sanders

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1977

Some Reactions of Alkyl Radicals

by Derek G Sanders

A

THESIS

PRESENTED FOR

THE DEGREE OF

DOCTOR OF PHILOSOPHY

OF THE

UNIVERSITY OF ST ANDREWS

ST ANDREWS

JANUARY 1977

Th 8862

Some Reactions of Alkyl Radicals : Abstract from a Thesis presented for the Degree of Doctor of Philosophy of the University of St Andrews by Derek G Sanders January 1977

The first part of the Thesis describes the work carried out in a study of the thermal decomposition of *n*-Propyl and *n*-fluoropropyl radicals. *n*-Propyl radicals were generated by the high temperature chlorination of propane. The chlorine atoms produced in this reaction can abstract a hydrogen atom from the primary position in the propane. The *n*-propyl radical thus formed can either react with molecular chlorine present in the system or, at the temperature used, decompose to form ethylene and a methyl radical. Approximate values for the rate parameters of this reaction were obtained.

A competitive technique for obtaining the rate parameters for the thermal decomposition of *n*-fluoropropyl radicals relative to the decomposition of the *n*-propyl radical was developed. Unfortunately due to the rapid decomposition of the starting material : 2,2-difluoropropane it was not possible to carry out these experiments.

During the course of this study kinetic data was obtained from the photolytic chlorination of propane, the thermal decomposition of *n*-propyl chloride and *sec*-propyl chloride and the competitive photolytic chlorination of propane and 2,2-difluoropropane.

The second part of the thesis describes a study of the comparison of the gas phase hydrogen abstraction reactions of trifluoromethyl and methyl radicals in the gas phase with *n*-butane, *n*-butyl fluoride and 1,1,1-trifluoropentane.

Trifluoromethyl radicals were generated by the photolysis of trifluoromethyl iodide. The relative selectivities of the radicals were obtained by the quantitative measurement of the iodides formed from the reaction of the alkyl radicals with trifluoromethyl iodide.

Methyl radicals were generated by the photolysis of azomethane. The radicals thus formed abstracted hydrogen atoms from one of the four reaction sites within the substituted butanes. The reactions were carried out in the presence of methyl iodide which acted as a chain propagator, the alkyl radicals formed abstracting iodine from the methyl iodide. The quantitative measurement of the alkyl iodides thus formed enabled the relative selectivities of the methyl radicals to be established.

The results obtained showed the effect of the substituents on the relative selectivities of the two radicals for the different reaction sites within the alkanes.

DECLARATION

I hereby declare that the work described in this thesis is a record of experiments carried out by me in the Chemistry Department of the University of St Andrews, that it is my own composition and that it has not been previously submitted for a higher degree.

Derek G Sanders

CERTIFICATE

I certify that Derek Graham Sanders, B.Sc., has spent ten terms of research work under my direction and that he has fulfilled the conditions of the Resolution of the University Court, 1967, No. 1 and as such he is qualified to submit this thesis for the degree of Doctor of Philosophy.

Professor Lord Tedder

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to Professor Lord Tedder and Dr. J.C. Walton for their continual encouragement and advice throughout the course of this work. I also thank Professor Lord Tedder and Professor P.A.H. Wyatt for facilities provided during the period of this research. A note of thanks must also go to Dr. H.W. Sidebottom for much useful advice.

I am indebted to the Science Research Council for a Research Studentship.

Finally my thanks to my wife, Maureen, for the typing of this thesis.

CONTENTS

INTRODUCTION

The breaking of a covalent bond can proceed in two different ways. The electrons forming the bond can be redistributed so that one part of the fragmented species has an overall negative charge and the other an overall positive charge. This process is known as *heterolytic fission* and is generally associated with organic reactions in the solution phase. Alternatively each fragment formed can acquire one of the bonding electrons resulting in two neutral free radicals. This process is known as *homolytic fission* and is frequently involved with reactions in the gas phase. Free radicals are extremely reactive species which usually have a very short lifetime.

The first authentic free radical was discovered by Gomberg [1] in 1900. He produced a substance which all experimental evidence led him to believe was triphenylmethyl radicals. This radical was in fact an example of one which exhibits a long lifetime.

The next important discovery was the demonstration of the existence of methyl radicals in the gas phase by Paneth and Hofeditz [2] in 1929. A stream of tetramethyl lead, in an inert carrier gas, was passed along a tube which was heated at a particular point. A film of lead was formed which subsequently disappeared when the tube was heated upstream from the original point, with the formation of a second lead film. The only product found at the end of the tube was tetramethyl lead. By altering the two points where the heating occurred Paneth and Hofeditz deduced that the lifetime of the methyl radicals was 10^{-3} secs at 2mm pressure.

The reactions of free radicals can be classified in the following manner.

Decomposition

e.g. $CH_3CH_2CH_2\cdot \longrightarrow CH_3\cdot + CH_2{=}CH_2$

Cyclisation

e.g.

Rearrangement

e.g. $CCl_3\dot{C}HCH_2Br \longrightarrow \dot{C}Cl_2CHClCH_2Br$

Combination (dimerisation)

e.g. $2PhCH_2\cdot \longrightarrow PhCH_2CH_2Ph$

Disproportionation

e.g. $2(CH_3)_3C\cdot \longrightarrow (CH_3)_3CH + CH_2{=}C(CH_3)_2$

Addition

e.g. $Br\cdot + CH_3CH{=}CH_2 \longrightarrow CH_3\dot{C}HCH_2Br$

Abstraction (radical transfer)

e.g. $Br\cdot + CH_3CH_2CH_3 \longrightarrow CH_3\dot{C}HCH_3 + HBr$

Most reactions involving radicals take the form of a chain process. Radicals are generated in a single initiation step. This is often followed by numerous propagation steps (no net loss or gain of radicals) and finally one or more termination steps (radical destroying).

An example of this is the chlorination of a hydrocarbon:

$Cl_2 + h\nu \longrightarrow 2Cl\cdot$ *initiation*

$Cl\cdot + RH \longrightarrow R\cdot + HCl$

$R\cdot + Cl_2 \longrightarrow R{:}Cl + Cl\cdot$ *propagation*

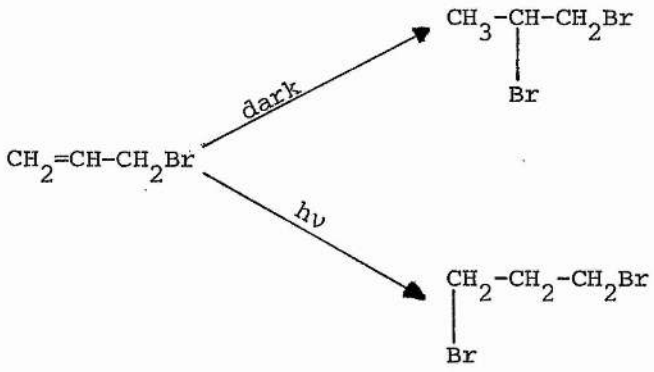
$2Cl\cdot + M \longrightarrow Cl_2 + M$

$2R\cdot \longrightarrow R{:}R$

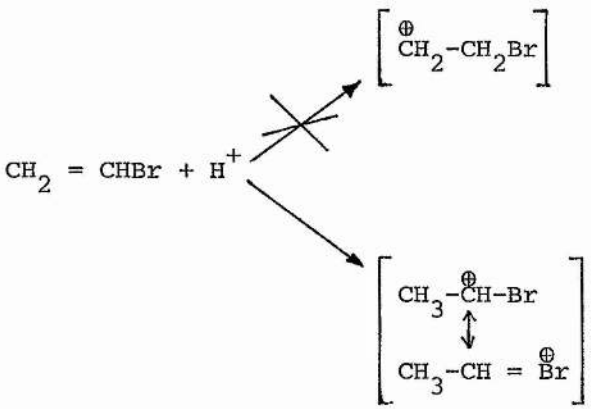
$Cl\cdot + R\cdot \longrightarrow R{:}Cl$ *termination*

Radical addition reactions have received much attention in recent years. The first qualitative work to be carried out was the study of the addition of hydrogen bromide to allyl bromide [3]. The study of this reaction by Kharasch [4] in America and Hey and Waters [5], independently, in England led to a proposed radical chain mechanism for the anti-Markovnikov addition of hydrogen bromide to olefins. Studies of the reaction carried out in the

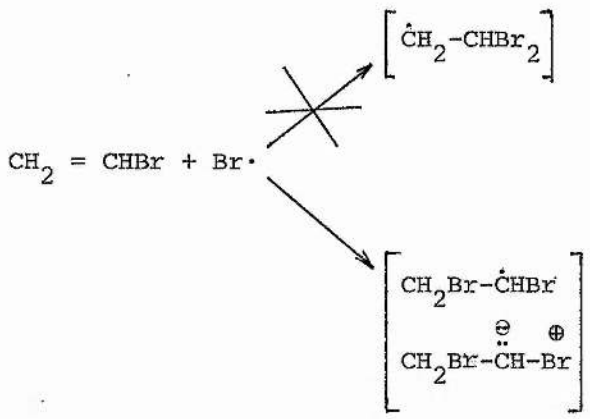
dark and in the absence of radical-producing materials led to the production of the expected Markovnikov product, 1,2-dibromopropane. This reaction proceeded slowly and by an ionic mechanism. In the presence of light however a rapid reaction occurred to produce 1,3-dibromopropane via a radical mechanism.



Of the many theories proposed for the orientation of the radical reaction, the most popular was that of Mayo and Walling [6]. In the ionic addition the product formed is the one which is produced by a mechanism which proceeds via the most stable carbonium ion.



Carbonium ions increase in stability in the order p < s < t. This is obviously responsible for the particular product in the ionic reaction. As the stability of radicals increases in the same order it can be deduced that the most likely product in the radical reaction is the one that proceeds via a secondary radical



The resonance stabilised intermediates seem to be responsible for the two different products in the addition of hydrogen bromide.

Much of the early work on the addition of methyl radicals to the olefinic double bond was carried out by Steacie [7]. Methyl radicals were generated by the photolysis of acetone in a static system. The rate of addition of the methyl radicals was measured relative to the rate of combination. A mass balance method was used in determining the rates which involved the analysis of the main products: methane, ethane and carbon monoxide. This method however can make no distinction between the formation of different adduct radicals in an unsymmetrical olefin.

Many different sources of methyl radicals have been used in addition studies. Raal and Danby [8] made use of the photolysis of

acetaldehyde when studying the addition to ethylene. The photolysis of acetone was again used by Endrenyi and Le Roy [9]. Biacetyl was photolysed by Cvetanovic and Irwin [10] to produce methyl radicals. They again used a mass balance method for determining reaction rates, each methyl radical being accounted for by a molecule of carbon monoxide. Again as in previous mass balance work it does not distinguish between the different adduct radicals in unsymmetrical olefins. Sangster and Thynne [11] used a similar method when studying the rate of methyl addition to tetrafluoroethylene. The thermolysis of di-*tert*-butyl peroxide has been extensively used as a source of methyl radicals [12,13,14].

In the work so far mentioned no attempt has been made to determine the relative rates of addition of methyl radicals to each end of an unsymmetrical olefin. Tedder, Walton and Winton [15] studied the addition of methyl radicals to fluoroethylenes in an attempt to obtain this particular result. Methyl iodide was present in the reaction vessel, reacting with the adduct radicals to form the two propyl iodides which were quantitatively analysed. The photolysis of methyl iodide however is not a suitable source of methyl radicals for kinetic results because the radicals produced are "hot". Azomethane was therefore used as a source of methyl radicals and excess methyl iodide added to promote a chain reaction. The results obtained showed considerably different trends from those obtained for addition of trichloromethyl [16] and heptafluoropropyl [17] radicals to the same olefin. This particular study was reinvestigated by Low, Tedder and Walton [14]. The same

source of methyl radicals was used as in the previous work although some studies were also carried out using the thermolysis of di-*tert*-butyl peroxide. In this study telomeric products were also formed and on correction for the presence of these species Arrhenius parameters were calculated which, in some cases, showed a significant difference from the previous work.

The work described in this thesis is divided into two sections. The first describes the work carried out in the investigation of the decomposition of halopropyl radicals in the gas phase. The work described in the second section forms part of a detailed study of the free radical substitution of aliphatic compounds.

PART I

THE THERMAL DECOMPOSITION OF *n*-PROPYL AND *n*-FLUOROPROPYL RADICALS

INTRODUCTION

Much of the information on the reverse radical decomposition of alkyl radicals comes from Bywater and Steacie's [18,19,20] investigations of the high temperature mercury photosensitized decomposition of alkanes.

Excited mercury atoms react with the alkane at room temperature to yield alkyl radicals and hydrogen atoms.

$$Hg^* + RH \longrightarrow Hg + R\cdot + H \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

The hydrogen atoms formed can then either combine or abstract a hydrogen from the alkane.

$$2H + M \longrightarrow H_2 + M \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

$$H + RH \longrightarrow H_2 + R\cdot \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

The alkyl radicals formed can either combine or disproportionate

$$2R\cdot \longrightarrow R_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4a)$$

$$2R\cdot \longrightarrow RH + R(-H) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4b)$$

or abstract from the alkane.

As the temperature is raised the alkyl radicals begin to decompose to form a hydrogen atom, methyl or ethyl radicals plus an olefin.

$$R\cdot \longrightarrow H + R(-H) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5a)$$

$$R\cdot \longrightarrow R'\cdot + R(-R'\cdot) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5b)$$

More of the original alkyl radicals are then generated by the attack of hydrogen or radical (R'·) formed on the alkane.

From the above reaction scheme it can be seen that the number of radicals removed by disproportionation and combination, (4), is equal to twice the rate of formation of hydrogen molecules, R_{H_2} produced at low temperatures.

$$k_4[R\cdot]^2 = R_{H_2}$$

$$[R\cdot] = (R_{H_2}/k_4)^{\frac{1}{2}}$$

The rate of decomposition of [R·] is equal to the rate of formation of R'H.

$$R_{R'H} = k_5[R\cdot]$$

Hence

$$\frac{k_5}{k_4^{\frac{1}{2}}} = R_{R'H}/R_{H_2}^{\frac{1}{2}}$$

or in the case where hydrogen is formed in the decomposition of the radical

$$k_5/k_4^{\frac{1}{2}} = R_{H_{2*}}/R_{H_2}^{\frac{1}{2}}$$

where $R_{H_{2*}}$ equals the total rate of formation of hydrogen less the rate of formation at low temperature.

Using this method values for Arrhenius parameters for the loss of methyl from the *n*-propyl (the reverse reaction of addition of methyl to ethylene) were obtained : $\log A = 9.2 sec^{-1}$ and $E = 20$ kcal mol^{-1}.

Kinetic data for the reverse radical addition was also evaluated by Masson [21]. On studying the photolytic decomposition of di-*n*-propyl ketone it was observed that above 161°C a chain reaction became significantly important of which one of the steps was the decomposition of a *n*-propyl radical.

$$n\text{-}C_3H_7\cdot \longrightarrow C_2H_4 + CH_3\cdot \quad \ldots\ldots\ldots \quad (6)$$

Although ethylene is also produced by the non-free radical primary decomposition of the ketone, the rate of formation of ethylene from the *n*-propyl radical was determined by the measurement of the products formed from the reactions of the methyl radicals (i.e. methane and ethane). A value for the activation energy of the decomposition was obtained (20 kcal mol^{-1}) which agreed favourably with the result obtained by Bywater and Steacie.

A method, first used by Gruver and Calvert [22], to study the decomposition of alkyl radicals is the photolytic chain-decomposition of aldehydes. Originally it was used to study the reactions of *sec*-butyl radicals produced by the photolysis of 2-methylbutanal.

Kerr and Trotman-Dickenson used the same method to study the decomposition of *n*-propyl radicals produced from the photolysis of *n*-butyraldehyde [23]. The rate of decomposition was determined by measuring the amount of methane plus ethane formed.

$$k_6/k_7^{\frac{1}{2}} = R_{C_2H_4}/R^{\frac{1}{2}}_{C_6H_{14}}$$

or

$$k_6/k_7^{\frac{1}{2}} = (R_{CH_4} + R_{C_2H_6})/R^{\frac{1}{2}}_{C_6H_{14}}$$

where k_7 is the rate constant for radical combination

$$2C_3H_7\cdot \longrightarrow C_6H_{14} \qquad \ldots\ldots\ldots \quad (7)$$

Arrhenius plots for each were obtained. The amount of hexane formed at higher temperatures was very small indeed. This problem was solved however by measuring the amount of propane formed in the step:

$$C_3H_7\cdot + C_3H_7CHO \longrightarrow C_3H_8 + C_3H_7CO\cdot \qquad \ldots\ldots \quad (8)$$

the relation between k_6 and k_8 being known. Using this method Kerr and Trotman-Dickenson obtained the following expression:

$\log k_6\ (\text{sec}^{-1}) = 11.7 - (25{,}200/2.303RT)$ for methane and ethane

and $\log k_6\ (sec^{-1}) = 11.4 - (25,300/2.303RT)$ for ethylene.

N.B. Throughout this thesis the Gas Constant R = 1.98 cal. $^{o}K^{-1}$.

The result for the calculation using methane is preferred as further reaction of the ethylene is likely to have occurred. Some correction has to be made for the small amounts of ethylene and methyl produced in one of the initiation steps:

$$C_3H_7.CHO \xrightarrow{h\nu} CH_3^{\cdot} + C_2H_4 + CHO\cdot$$

It is to be expected that the rate of decomposition of *n*-propyl radicals is dependent upon the rate of energy transfer, and consequently, the pressure of reactants. This was in fact confirmed during the work by increasing the amount of aldehyde by three-fold and finding an increase in rate by a factor of 1.6. A small increase was also obtained by the addition of carbon dioxide. Kerr and Trotman-Dickenson suggested that the low A-factor may in fact be due to the slow rate of energization of the *n*-propyl radicals and that the high pressure A-factor might well be over 10^{12} sec^{-1}. The value for the activation energy is considerably higher than the two previous values mentioned. This could not be explained due to lack of detailed information in the previous work.

The need for small corrections for the amount of ethylene and methane required in the previous work was overcome by Calvert and Sleppy [24]. They produced *n*-propyl radicals from *n*-butyraldehyde by using azomethane as a photoinitiator.

$$(CH_3)_2N_2 \xrightarrow{(3660\ \text{Å})} 2CH_3\cdot + N_2$$

These methyl radicals formed initiate the thermal decomposition of the aldehyde. In this case the decomposition can obviously only be followed by the measurement of the ethylene formed. The result obtained,

$$\log k = 15.8 - (34{,}900/2.303RT) \text{ sec}^{-1}$$

is in poor agreement with the previous studies.

Kerr and Calvert[25] attempted to resolve the conflict of estimates of the rate constant for the decomposition of *n*-propyl radicals which they had separately obtained. Kerr and Trotman-Dickenson stated that the rate constant was a function of pressure and indeed the experiments carried out by Calvert and Sleppy had been executed with approximately six times more total concentration of reactants suggesting that a higher value for the rate constant would be attained. This would by no means account for the large discrepancies however, and further work was carried out using a third source of *n*-propyl radicals, azo-*n*-propane. Photolysis and pyrolysis of azo-*n*-propane was carried out. The amount of ethylene produced was always much greater than that of methane. This was found to be caused by addition of methyl radicals to the azo-*n*-propane double bond rather than other sources of ethylene existing. The results obtained:

$$\log k = 15.36 - (34{,}500/2.303RT) \text{ sec}^{-1}$$

for a concentration approximately the same as that used by Kerr and Trotman-Dickenson. It was suggested that the difference between the Arrhenius parameters obtained in their study was due to the

fact that they were unable to measure the hexane formed directly and that some error was incurred by this. Although the Arrhenius parameters for this work were in excellent agreement with the previous work of Calvert and Sleppy, the differences in the rate constants in this case were thought to be a result of the large pressure differences between the two systems. An attempt was made to put this pressure dependence on a quantitative basis. This proved experimentally not possible although the qualitative observations in this work show that the difference in pressure is definitely a factor in the difference between the rate constants derived in the two studies.

Back and Takamuku [26] reinvestigated the mercury-photosensitised decomposition of propane which had been originally carried out by Steacie [18,19,20]. The results obtained however were very similar to the results originally obtained even with the use of improved analytical techniques.

Lin and Laidler [27] studied the decomposition of propane sensitised by azomethane. The rate of decomposition of the *n*-propyl radical was again measured using the relationship

$$R_{C_2H_4}/R^{\frac{1}{2}}_{n\text{-}C_6H_{14}} = k_6/k_7^{\frac{1}{2}}$$

It was found that the ratio, as expected, was independent of the amount of azomethane in the system and that it is also independent of pressure. Taking log k_7 as 16.34 $dm^3\ mol^{-1}\ sec^{-1}$ the expression

$$\log k_6(sec^{-1}) = 13.54 - (31,400/2.303RT)$$

was obtained. The result gives a much higher value for the activation

energy than that reported by Steacie or Back and lower than the more favoured values obtained by Calvert. The value for the rate constant in Laidler's work however is seven times smaller than the value obtained by Calvert and Sleppy [24], at 300°C. It is suggested that this is due to the presence of the radicals, $\cdot CH_2CH_2CH_2CHO$ and $CH_3CH_2\dot{C}HCHO$ which could decompose to give ethylene and methyl radicals. No complications are expected from the decomposition of *sec*-propyl radicals in this system as the rate of decomposition to give ethylene and methyl radicals is slower by a factor of 10^3.

The first study of the decomposition of *n*-propyl radicals over a pressure as well as a temperature range was carried out by Papic and Laidler [28] in order to obtain the limiting behaviour at low and high pressures, *n*-propyl radicals were produced by the mercury-photosensitized decomposition of propane. The rate of formation of ethylene was proportional to propane pressure at low pressures and became independent at high pressures, the limiting pressure increasing significantly with increasing temperature. A value for the limiting high pressure rate constant is given by the expression

$$\log k^{\infty}(sec^{-1}) = 14.40 - (32,600/2.303RT)$$

and for the limiting low pressure rate constant by the expression

$$\log k^{o} \ (dm^3 \cdot mol^{-1} \ sec^{-1}) = 10.40 - (17,000/2.303RT)$$

The previous low values for the activation energies were almost certainly due to the fact that the reactions were carried out in the pressure-dependent region.

Much work has been carried out in the laboratory on the addition of methyl and halomethyl radicals to ethylene and fluoroethylenes. For the reaction

$$CH_3^{\cdot} + CH_2 = CH_2 \longrightarrow {}^{\cdot}CH_3CH_2CH_2^{\cdot} \qquad (9)$$

a preferred value for the rate constant [31] (k_9) is

$$\log k_9 = 8.52 - (7.7/2.303RT)\,\text{sec}^{-1}$$

The equilibrium constant for the above reaction can be written in the form

$$K = k_9/k_{-9}$$

This value can be estimated from thermodynamic data. The experimental value for k_9 obtained for the addition of radicals to an olefinic double bond can therefore be checked if a value for k_{-9} can be experimentally obtained. Alternatively the validity of the estimated value of the equilibrium constant can be verified. The overall aim however was the determination of D(C-C) in the propyl radicals with a view to correlating this with the activation energies for the addition reactions to see if D(C-C) is a major factor in addition reactions. The work described in this section of the thesis is an attempt to determine the rate parameters for the decomposition of halopropyl radicals to this end.

EXPERIMENTAL

MATERIALS

Chlorine (ICI) and propane (Matheson research grade) were both purified by several trap to trap distillations before storing in two litre glass bulbs with side-arms. Bromine (Fisons S.L.R.) was introduced onto the vacuum line as required in a glass tube with a greaseless cone fitting. This also was purified by trap to trap distillation. *n*-Propyl chloride and *sec*-propyl chloride (Hopkin and Williams) were both purified by use of a Pye-Unicam 105 preparative G.L.C. apparatus. They also underwent further purification by trap to trap distillation on introduction to the vacuum line where they were stored in glass tubes. The 2,2-difluoropropane was prepared as follows.

Preparation of 2,2-Difluoropropane [29,30]

The reaction was carried out in a large stainless steel bomb. Acetone (29g, AR) was placed into the reaction vessel and the bomb was assembled. The vessel was cooled in a dry ice/acetone mixture to $-70^{\circ}C$ and the apparatus was degassed using a rotary vacuum pump. Sulphur tetrafluoride (67g) was then frozen into the reaction vessel and the valve for the whole assembly closed. The reaction vessel was then heated up to $100^{\circ}C$ (approx.) by immersion into steam heated water. The reaction was carried out for twenty four

hours at this temperature.

The gaseous products were then passed through three gas washing bottles containing a solution of sodium hydroxide (5M). This removed any unreacted sulphur tetrafluoride and acetone present as well as the hydrogen fluoride and thionyl fluoride produced. The remaining gas was collected in a trap immersed in a dry ice/acetone mixture at $-75^{o}C$.

The product was transferred to the vacuum line and further purification by trap to trap distillation was carried out before the gas was introduced into a two litre storage bulb. The product was confirmed as 2,2-difluoropropane by mass spectrometry and G.L.C. analysis, which also revealed that no impurities were present.

APPARATUS

The experiments were carried out on a conventional "Pyrex" vacuum line with Jencons greaseless fittings (Figure 1). The vacuum in the system was maintained with an Edwards 'Speedivac' silicone oil diffusion pump backed by a rotary pump. The pressure of the reactants in the system was measured with a glass spiral gauge. A zero-reading was taken by bleeding air into one side of the gauge which also recorded the pressure on a mercury manometer. The glass bulbs I(122ml), and II(299ml) were used for measuring quantities of reactants along with the small and large manifold (308ml, 742ml), reaction vessel III(310ml), and mixing bulb V(Figure II, 304ml). The

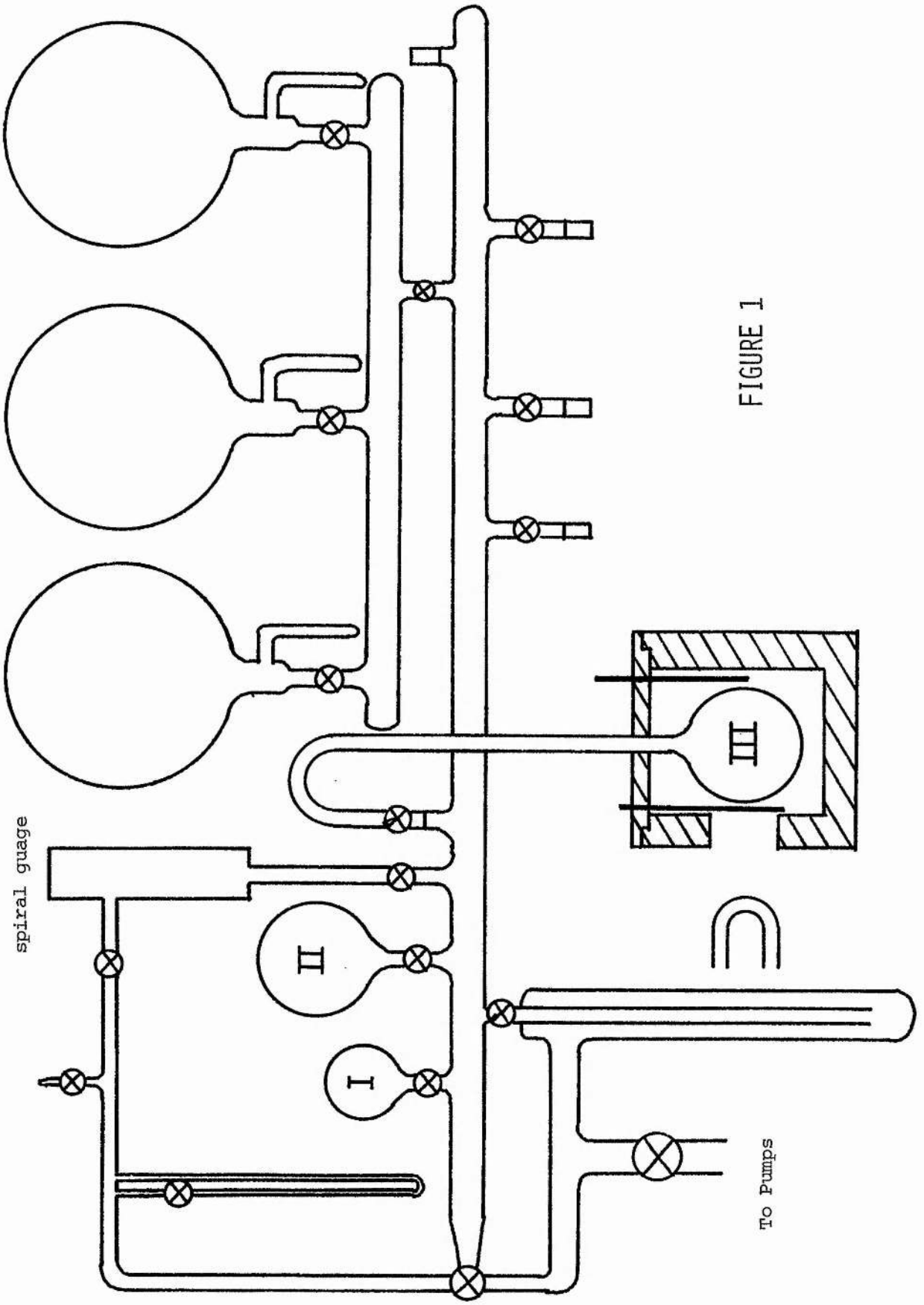


FIGURE 1

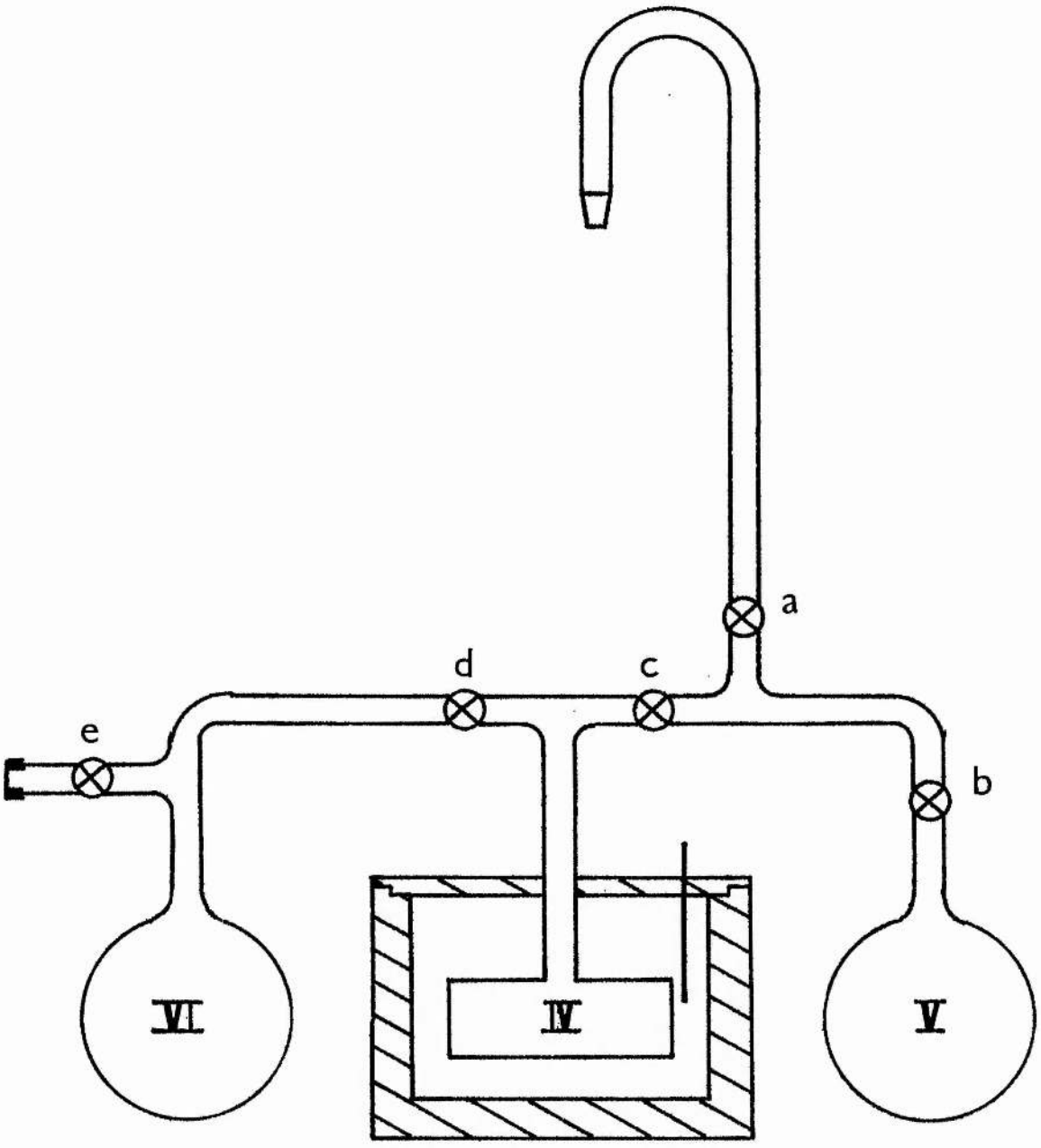
volume of bulb I was accurately determined by measuring the weight of water held. This value was then used as a reference in finding the volumes of all other parts of the apparatus by expansion of air and measuring the change of pressure on the manometer.

The reaction vessel used in the photolysis experiments (III) was spherical (310ml) and made of "Pyrex" glass which acted as a filter for light with a wavelength of less than 2800Å. The reaction vessel was connected to the main manifold via 2mm capillary tubing to minimise the volume of reactants outside the reaction chamber.

The furnace used in the photolysis experiments consisted of a spherical aluminium chamber with a 2½" circular hole in the side to allow the passage of light. This chamber was heated by electrical elements around the walls and base and insulated with asbestos tape. A "Variac" transformer (0→250 volts) was used as the power source and the temperature in the furnace was measured with a mercury in glass thermometer. The light source was a 150 watt tungsten lamp placed close to the circular hole. A cylindrical quartz reaction vessel containing a dilute copper sulphate solution (5%) was placed inbetween the light and the reaction vessel to act as a filter for infra-red radiation. A moveable shutter was also incorporated into the furnace.

The thermolysis reaction system is shown in Figure 2. The cylindrical reaction vessel IV(202ml) was made of quartz and was connected to a small manifold (29ml) and also to a gas sampling bulb VI(247ml) via greaseless taps. The furnace was part of a Perkin-Elmer F11 Gas chromatograph with minor modifications. The

FIGURE 2



temperature was measured with a Ni-Cr/Ni-Al thermocouple and Comark electronic thermometer.

The main manifold and all parts of the apparatus which contained reactants after mixing were 'blacked out' with adhesive tape and aluminium foil. The vacuum was monitored at all times by the use of a high frequency tesla coil.

PROCEDURE

Before each run was carried out the apparatus was pumped down for at least one hour with the trap immersed in liquid nitrogen and the furnace in place around the reaction vessel.

Photolytic chlorination of propane

The reactants were thoroughly degassed before each separate run. The furnace was removed from the reaction vessel and the 'Variac' was set to the voltage required for the particular temperature of the run. Propane was allowed to expand from the storage bulb into the manifold, spiral gauge and reaction vessel. When the correct pressure had been obtained the reaction vessel was isolated and the propane condensed back into the storage bulb by cooling with liquid nitrogen. The line was then pumped down for a short period.

This process was repeated for chlorine. This time however the reaction vessel remained isolated and the chlorine was introduced in to one of the small measuring bulbs. Because it was not possible to measure small pressures using the spiral gauge and manometer, larger pressures of chlorine were measured into the small bulb. This was then isolated and the excess chlorine condensed back into the storage bulb as previously described. The chlorine in the measuring bulb could then be expanded into whatever volume was necessary to attain the required pressure. The measuring bulb was again isolated, the excess chlorine pumped away, and the required amount of chlorine condensed into the reaction vessel, a tesla coil being used to make sure it had all frozen down.

The condensed contents were then pumped down, warmed up to room temperature, and again condensed and pumped down before the reaction vessel was heated in the furnace. When the temperature had equilibriated, which generally took about half an hour, the lamp was switched on and the shutter lifted.

After photolysis had taken place for the required length of time, the lamp was switched off and the reaction mixture was condensed into an evacuated glass tube attached to the main manifold. At least half and hour was allowed for condensation to occur. The tube was then removed from the line and stored in liquid nitrogen for analysis.

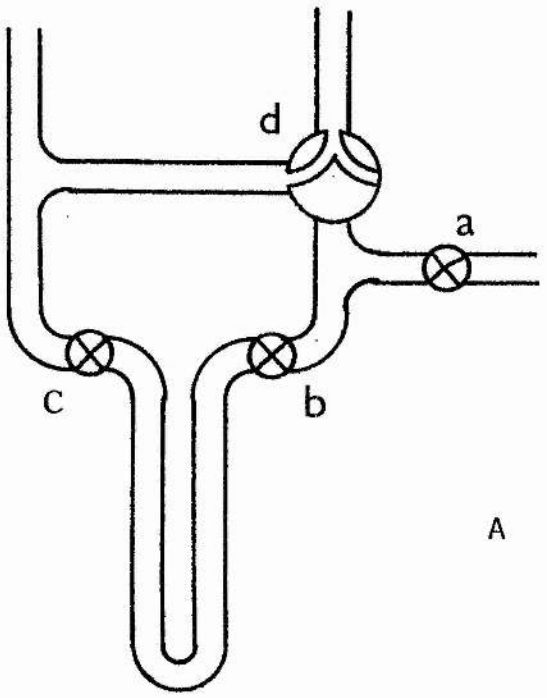
Photolytic chlorination of propane and 2,2-difluoropropane

Basically the same technique and apparatus was used as in the previous section. In this particular work it was vital that the

relative amounts of propane and 2,2-difluoropropane were measured accurately. To obtain this, both hydrocarbons were expanded into the same measuring bulb so as to eliminate any errors arising from the different volumes. In this particular series of experiments the reaction products were collected in a sampling vessel (Figure 3b) for analysis.

High temperature chlorination of propane

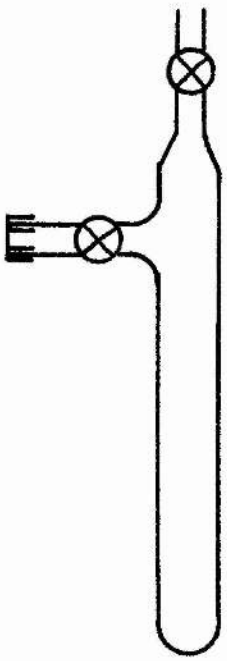
The procedure for this reaction was very similar to that used in the photolytic runs. The preparation of the vacuum line and measurement of reactants were the same. Care had to be taken when measuring the pressure of chlorine used because the exact amount used needed to be known. Instead of using the reaction vessel for measurement of one reactant and finally mixing of all reactants, the mixing vessel was now used (Figure 2, V) with the taps (a) and (b) open and (c) closed. The reaction vessel was permanently enclosed by the oven and a much longer period of time was needed for the temperature to equilibriate. When the reactants had been mixed and degassed taps (b) and (d) were closed and (c) opened. The reactants were allowed to reach room temperature, tap (a) was closed and (b) opened followed almost immediately by the closing of (c). The residual reactants were then immediately pumped away.



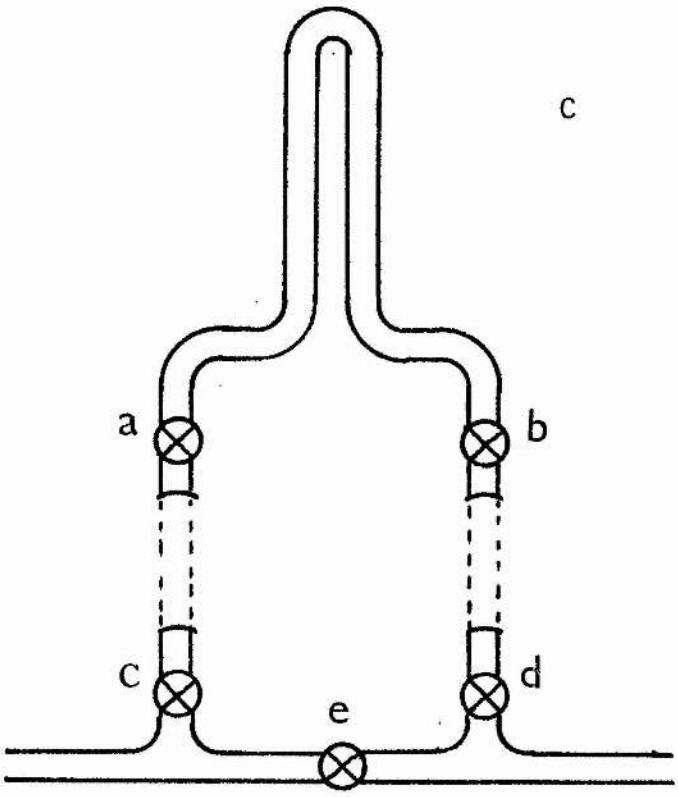
A

FIGURE 3

B



C



The procedure from this point changed during the course of the work. Originally the reactant mixture was returned to the mixing bulb (V) after the required length of time had elapsed. This was carried out by closing tap (a) and opening tap (c) with the mixing bulb immersed in liquid nitrogen. At least one hour was allowed for the products to distill over although even after this period of time some discharge still showed up when the tesla coil was applied. This was due to the presence of methane which will not completely distill over at liquid nitrogen temperature.

The method and apparatus was therefore modified so as to cope with the problem. The sampling vessel VI was added to the side of the reaction system. After reaction had preceded for the desired length of time tap (d) was opened and closed again almost immediately.

The same procedure as described above was also used in the bromination of propane, and the competitive chlorination of propane and 2,2-difluoropropane.

Thermal decomposition of *n*-propyl chloride and *sec*-propyl chloride

The same method for measuring the gases as previously described was used. The measured gases were condensed in the mixing bulb (Figure 2, V) and degassed. They were then introduced into the reaction vessel again as previously described. The reaction products were collected by distillation into the mixing bulb after reaction had taken place.

ANALYSIS

Photolytic chlorination reactions

The analysis of these runs were carried out on a gas chromatograph with a gas density balance detector. A 12ft glass Pye-Unicam preparative colume was used. The packing material consisted of a 25% (w/w) tritolylphosphate stationary phase on 60/100 mesh 'Embacel' support. The injections were made using a 10µl Hamilton syringe (N 701) which was cooled in liquid nitrogen. A standard Pye 104 series injection port was incorporated into the gas chromatograph. Oxygen free nitrogen was used as a carrier gas.

The gas density balance detector was the same type as used in a Griffin and George D6 gas chromatograph. This detector is a dynamical analogue of the Wheatstone bridge, the analogues of the resistances being the two legs of the density balance and the analogue of the ammeter, a sensitive anemometer. When both legs of the density balance consisted of carrier gas alone, there was no flow through the anemometer. When a sample was eluted from the column, the densities of the gases in the two legs were different, and the rate of gas flow through the anemometer was proportional to the differences in densities. The electrical response from the anemometer was amplified and fed into the recorder unit which incorporated a Honeywell Brown 1 millivolt potentiometric recorder, so producing a chromatogram.

When a weight q of a sample of molecular weight M passes through the density balance in a stream of carrier gas, molecular weight m,

then the measured peak area A on the chromatogram is given by

$$q = kA \frac{M}{M-m}$$

where k is a constant for the instrument. Hence the concentration of the sample is given by

$$\frac{q}{M} = k \frac{A}{M-m}$$

The areas of the peaks were measured using either a 'Dupont' 310 Curve Resolver or a fixed arm planimeter.

The analysis of the runs of the photolysis of 2,2-difluoropropane, propane and chlorine was carried out in a very similar manner. In this case however, the sample was a gas which had been collected in a special sample tube (Figure 3 (b)). The conditions of analysis remained the same i.e. carrier gas, column flow-rate and temperature. The gas was introduced into the column by the use of a 1 ml disposable syringe and needle.

High temperature reactions

The analysis of products formed from the high temperature chlorination of propane was far from straight forward and many different techniques were tried without much success. The method of analysis first used was the same as previously described, injection of liquid samples and the use of a gas density balance detector. Squalane (25%), tritolyl phosphate (25%) and silicone

oil (20%) were all tried under various conditions in order to separate small amounts of propylene from the bulk of propane. Very little success was achieved but with the use of the 'Dupont' 310 curve resolver a quantitative reproducible value was possible.

The products from these reactions were highly volatile and the accurate sampling of cooled liquids became impossible. A gas sampling method was devised using the apparatus in Figure 3(c).

As previously mentioned, after reaction the reactants were condensed into the side mixing bulb (Figure 2, V). With tap (b) closed the reactants were allowed to warm up to room temperature, the rest of the system being pumped down. Taps (a) and (c) were then closed and tap (b) opened for a few seconds. This allowed a portion of the reactants to be separated into the manifold enclosed by the three taps. This was in fact a convenient amount of sample for analysis.

The U-tube part of the apparatus in Figure 3 (c) was attached to the vacuum line via one of the greased ball and socket joints. This was pumped down completely with one of the taps closed to the atmosphere and the other open to the main manifold of the vacuum line. When a high vacuum had been obtained, a Dewar of liquid nitrogen was placed around the U-tube and tap (a) was opened allowing the small amount of reactants to distill into the U-tube. At least forty five minutes were allowed for complete condensation to occur, after this had passed the taps on the U-tube were closed and the tube removed from the vacuum line.

The second part of the apparatus (Figure 3 (c)) was incorporated into the gas chromatograph. The nitrogen carrier gas passed through

it immediately before entering the oven. When the U-tube was not connected taps (c) and (d) were closed and tap (e) was open thus allowing uninterrupted flow of carrier gas to the column. The U-tube was clamped in place and the taps (c) and (d) opened. A few minutes were allowed for the carrier gas to purge any air inbetween the two sets of taps and also for the contents of the U-tube to warm up. The tap (e) was then closed and taps (b) and (a) immediately opened, the carrier gas thus purging the contents of the U-tube into the chromatograph. This method of analysis proved far more satisfactory than the previous method of analysing the liquid phase. A major problem arose however for the analysis of ethylene. It was expected that this gas would be a major product in these particular reactions and yet none was detected. As can be seen from the expression

$$q/m = k\ A/(M-m)$$

the sensitivity of the detector is proportional to the difference in the molecular weights of the eluant and the carrier gas. Nitrogen carrier gas therefore is useless in the analysis of ethylene and very poor for the analysis of ethane, another expected product.

Of the gases with a molecular weight lower than nitrogen, helium seemed the most suitable although the use of this also had problems. The heater filament in the detector required a current of 1.9 amps to keep it on the 'black heat' region. The detectors in fact were designed for the use of nitrogen and if another carrier gas was used a different heater current was required. This current could be

calculated using the expression

$$\text{Current} = 1.9 \frac{(\text{Mol. Wt. of Nitrogen})^{\frac{1}{2}}}{(\text{Mol. Wt. of Carrier gas})^{\frac{1}{2}}}$$

for hydrogen this worked out at over five amps which was impossible to achieve. For helium the expression became

$$\text{Current} = 1.9 \sqrt{28/8} \quad = 3.6 \text{ amps}$$

This figure was also impossible to achieve without radical changes being made to the chromatograph. Helium therefore was used with the 1.9 amps heater current supplied for use with nitrogen carrier gas. The sensitivity of the detector was greatly reduced because of this and although it was possible to detect ethylene and ethane, the amounts produced were minimal and the method not practical.

A method of quantitative analysis using mass spectrometry was attempted to measure the amounts of propylene, ethylene, ethane and methane formed. The sampling tube (Figure 3 (b)) was used to collect a portion of the reaction products. This was then attached to an A.E.I. MS 902 mass spectrometer via a gas sampling system incorporated into it. Although this technique would be satisfactory for some mixtures, a characteristic peak for each compound could not be found which was large enough to allow quantitative measurements and was not present in other compounds present.

The only way of solving the analytical problems seemed to be in the use of a Flame Ionisation Detector. This is far more sensitive than a gas density balance detector although a response factor for each individual component in a mixture has to be found by calibration

with known mixtures of the components. It was proposed that an in-line sampling system should be used as no problems could be envisaged in building it and there are many obvious advantages resulting from its use.

A Perkin-Elmer model F11 gas chromatograph was used incorporating a temperature programmer control for the oven. The gas sampling and injection system designed for this system is shown in Figure 3(a). Hydrogen burnt in the detector also served as the carrier gas. It was therefore important to keep a constant flow of hydrogen so that the flame was not extinguished. Tap (d) on the diagram is a three-way greased, and sprung tap, (a), (b) and (c) are all greaseless. With tap (d) in the position shown on the diagram the carrier gas could by-pass the U-tube. Tap (c) was closed and tap (b) and (a) were opened and the system pumped out. A small part of the reaction products were isolated as previously described. When a good vacuum had been obtained, a dewar of liquid nitrogen was placed around the U-tube and the reaction products were condensed into the tube. At least half an hour was given for this to complete and then taps (a) and (b) were closed and the U-tube tube warmed up to room temperature. Tap (d) was rotated through ninety degrees in a clockwise direction and taps (c) and (a) opened simultaneously. The hydrogen carrier gas purged the U-tube and carried the sample into the column.

The problem of separation of methane, ethylene and ethane and also propylene, propane and methyl chloride (if it was formed) had not yet been solved. The squalane column (12', 25%) solved the problem of methane, ethylene, ethane separation but was poor for

the two propyl chlorides. A commercial packing material 'Chromosorb 102' was tried and found to give good results when incorporated with temperature programming.

The detector had to be calibrated for all likely reaction products. Calibration mixtures were made up in a 500ml glass bomb fitted with a rubber septum cap. Gases were introduced into the bomb with a 5ml glass syringe. A 10µl Hamilton syringe was used for liquids. When complete mixing had occurred 1ml samples were taken from the bomb and injected into the chromatograph. The calibration was carried out relative to ethylene and therefore each calibration mixture contained ethylene and up to three other components. The reproducibility of the method was first tested by introducing 5ml of ethylene into the glass bomb, allowing it to mix and then injecting several 1ml samples. The reproducibility was found to be excellent for consecutive injections. The results of the calibrations of the propyl chlorides proved unsatisfactory and many calibration mixtures had to be made up in order to obtain a mean value of some accuracy. Chlorinated products often give dubious results when a flame ionisation detector is used. This is usually caused by scavenging by the chlorinated compounds on the detector causing an enhancement of the signal.

The factors were calculated by dividing the peak area of the ethylene by the peak area of the particular compound, an allowance had to be made for the amount of sample placed into the glass bomb.

$$\text{Response factor} = \frac{A_{(C_2H_4)}}{A_{(X)}} \times \frac{[X]}{[C_2H_4]}$$

TABLE 1/1

Calibration Factors for Perkin Elmer F11 Flame Ionisation Detector

Compound	Multiplication factor (w/v)
Methane	1.00
Ethylene	1.00
Ethane	1.00
Propane	1.02
Methyl Chloride	4.02
sec-Propyl Chloride	7.42
n-Propyl Chloride	7.73

It became increasingly obvious that methane was one of the major products and that under the conditions used to transfer reaction products not all of it would be accounted for. Another system of sampling was therefore devised using the sampling bulb VI (Figure 2).

After reaction for the required length had occurred, tap (d) was opened (the sampling bulb having previously been evacuated) for

a few seconds then closed. The space between the septum cap and the tap (a) was evacuated using a 5ml syringe. Tap (a) was then opened and a sample taken with a 5ml syringe by pulling out the plunger to its maximum possible extent, closing (a) and allowing the plunger to return to the position giving a pressure equal to atmospheric pressure inside the syringe. This sample was then injected into the F11 chromatograph and analysis carried out as previously described.

In the thermal decomposition of *sec*-propyl chloride the reaction products were condensed over into a cold finger attached to the main manifold and previously pumped down. Forty five minutes were allowed for all products to condense and the cold finger was removed from the line. Analysis of the cooled liquid was carried out using a Hamilton 10µl syringe (N 701) cooled to liquid nitrogen temperature. A chromatograph with gas density balance was used.

For the experiments with *n*-propyl chloride, sampling and in-line analysis identical to that already described for the high temperature chlorination of propane was used.

IDENTIFICATION OF PRODUCTS

Photolytic reactions

The identification of *n*-propyl chloride and *sec*-propyl chloride was straight forward as authentic samples were readily available. These authentic samples were added in turn to a sample of reaction products prior to analysis. An enhancement of a peak occurred and this was therefore suspected of being that particular chloride. Another analysis was then carried out using a different column and analytical conditions. The same peak was enhanced confirming its identification.

This procedure was carried out for the identification of both propyl chlorides. The identification of 1-chloro.2,2-difluoropropane was not so easy, and confirmation of the suspected peak had to be carried out by mass spectrometry.

The mass-spectra were obtained on an A.E.I. MS 902 mass spectrometer with a Pye 104 gas chromatograph, used to separate the products, integrated into the equipment. A 12ft, (25%) tritolyl-phosphate glass column was used. Mass-spectra were recorded when the signal from the chromatograph reached a maximum.

High Temperature Reactions

The products of the reactions with propane were all identified by the use of authentic samples in the way previously described. Only two runs were carried out with 2,2-difluoropropane and a mass spectrum was used to identify the one very large product: 2-fluoropropene. For the runs carried out using bromine instead of chlorine, no identification of products was carried out.

DETAILS OF REACTIONS

Photolytic Chlorination of Propane

Analysis by gas chromatography

25% tritolyphosphate on 60/100 Embacel (12', glass),

nitrogen carrier gas, flow rate 50 mls/min.

oven temperature 100°C.

Irradiation time 120 secs

Reactant Pressure Chlorine 10mm

Propane 100mm

Temp (°C)	[*sec*-PrCl]/[*n*-PrCl]
16	1.266
24.5	1.331
44	1.186
45	1.118
59	1.211
77	1.149
100	1.102
122	1.094

A least squares plot of log 3[*sec*-PrCl]/[*n*-PrCl] against $10^3/T$ gave a gradient of 0.072 (± 0.040) and an intercept of 0.338 (± 0.014)

TABLE 1/2 : VARIATION OF TEMPERATURE

Thermal decomposition of *n*-Propyl chloride

Analysis by gas chromatography

Chromosorb 102 (6', S.S.), hydrogen carrier gas, 40mls/min, oven temperature 100°C

Reaction time 8 min

Pressure of *n*-PrCl 50mm

Temp (°C)	$[\text{Propene}]_f^*$	$[n\text{-PrCl}]_f^*$
360	50	22,000
430	30	3,266
450	50	684
465	36	1,190

A least squares plot of log k against $10^3/T$ gave a gradient of 13.10 (± 1.56) and an intercept of 13.95 (± 1.10).

TABLE 1/3 : VARIATION OF TEMPERATURE

* Relative concentrations

Thermal decomposition of *sec*-propyl chloride

Analysis by gas chromatography

25% tritolylphosphate on 60/100 Embacel (12', glass),

nitrogen carrier gas (flow rate 50mls/min),

oven temperature 60°C.

Pressure of *sec*-PrCl 20mm

Temp (°C)	$[sec\text{-PrCl}]_f^*$	$[\text{Propene}]_f^*$	time (secs)
420	1.31	47.4	1680
400	2.97	44.2	1800
380	1.83	43.7	1800
360	32.4	33.4	1800
340	40.1	25.4	1800
300	45.6	16.0	1800

A least squares plot of log k against $10^3/T$ gave a gradient of -4.32 ($\pm$ 1.23) and intercept of 4.28 ($\pm$ 0.78).

TABLE 1/4 (a) : VARIATION OF TEMPERATURE

* Relative concentrations

time (secs)	$[sec\text{-PrCl}]_f$	$[\text{Propene}]_f$
0	66.4	-
900	40.5	17.3
1800	38.2	24.6
2700	37.9	29.7
3600	35.2	31.4
4620	32.2	34.4
5400	33.3	37.6

A least squares plot of log $[sec\text{-PrCl}]_i/[sec\text{-PrCl}]_f$ against time gave a gradient of 0.214 ($\pm$0.012) and an intercept of 0.197 ($\pm$0.034). A least squares plot of log $[sec\text{-PrCl}]_f$ against time gave a gradient of -0.216 ($\pm$0.012) and an intercept of 1.63 ($\pm$0.033).

TABLE 1/4 (b) : VARIATION OF TIME (Temperature = 350^{o}C)

High temperature chlorination of propane

Analysis by gas chromatography

Chromosorb 102 (6', S.S.), hydrogen carrier gas, oven temperature 30°C (10min) ——> 100°C (4°C/min), initial flow rate 40mls/min.

Reaction time 5 mins

Reactant Pressure Chlorine 2.5mm (10^{-4} moles)

Propane 50mm

Temp (°C)	[*n*-PrCl]/[C_2H_4]
320	450
340	430
360	100
375	100
385	95
410	32
415	16
420	20
430	5.6*
440	2.4*

* not used in plot due to decomposition of *n*-PrCl

A least squares plot of log 10^4 [*n*-PrCl]/[C_2H_4] against 10^3/T gave a gradient of 5.93 (± 1.01) and an intercept of -3.26 (± 0.65).

TABLE 1/5 : VARIATION OF TEMPERATURE

Competitive photolytic chlorination of propane and 2,2-difluoropropane

Analysis by gas chromatography

25% tritolylphosphate (12', glass), nitrogen carrier gas, oven temperature 100°C, flow rate 60mls/min

Reaction time 600 secs

Reactants 2,2-difluoropropane 1.62×10^{-3} mol

propane 5.29×10^{-5} mol

chlorine 2.91×10^{-5} mol

Temp (°C)	$\frac{[CH_3CH_2CH_2Cl] \times [CH_3CF_2CH_3]}{[CH_3CF_2CH_2Cl] \times [CH_3CH_2CH_3]}$ (X)
103	7.67×10^2
125	5.07×10^2
147	4.99×10^2
172	3.09×10^2
196	2.74×10^2

A least squares plot of log X against $10^3/T$ gave a gradient of 0.841 ($\pm$0.277) and an intercept of 0.636 ($\pm$0.116).

TABLE 1/6 : VARIATION OF TEMPERATURE

RESULTS AND DISCUSSION

The decomposition of the *n*-propyl radical has been extensively studied. Therefore a method for the study of the decomposition of halopropyl radicals can be examined by the investigation of *n*-propyl radicals and comparing the results obtained. This was in fact the first objective. The high temperature chlorination of propane was used as a source of *n*-propyl radicals.

The reaction scheme envisaged was as follows:

$$Cl_2 + M \rightleftharpoons 2Cl\cdot + M \qquad (1)$$

$$Cl\cdot + C_3H_8 \longrightarrow CH_3CH_2CH_2\cdot + HCl \qquad (2a)$$

$$\longrightarrow CH_3\dot{C}HCH_3 + HCl \qquad (2b)$$

$$Cl_2 + CH_3CH_2CH_2\cdot \longrightarrow CH_3CH_2CH_2Cl + Cl\cdot \qquad (3a)$$

$$Cl_2 + CH_3\dot{C}HCH_3 \longrightarrow CH_3CHClCH_3 + Cl\cdot \qquad (3b)$$

$$CH_3CH_2CH_2\cdot \longrightarrow CH_2{=}CH_2 + CH_3\cdot \qquad (4)$$

$$CH_3\cdot + Cl_2 \longrightarrow CH_3Cl + Cl\cdot \qquad (5)$$

$$Cl\cdot + CH_2{=}CH_2 \longrightarrow ClCH_2\dot{C}H_2\cdot \qquad (6)$$

$$ClCH_2CH_2\cdot + Cl_2 \longrightarrow ClCH_2CH_2Cl + Cl\cdot \qquad (7)$$

It was found however that reactions (5), (6) and (7) did not occur to a measurable extent.

The rate constant required is the one for the decomposition of the propyl radical, k_4. The rate of formation of methyl radicals can be expressed as

$$\frac{d[CH_3\cdot]}{dt} = R_{CH_3\cdot} = k_4[CH_3CH_2CH_2\cdot] \qquad (8)$$

If one presumes, as in the above reaction scheme, that the only other fate of *n*-propyl radicals is the reaction with molecular chlorine, it should be possible to compare the rate of chlorination of *n*-propyl radicals with their rate of decomposition. In practice however the *n*-propyl radicals could undergo any of the following three reactions.

$$CH_3CH_2CH_2\cdot + Cl\cdot \longrightarrow CH_3CH_2CH_2Cl \qquad (9)$$

$$2CH_3CH_2CH_2\cdot \longrightarrow CH_3CH_2CH_2CH_2CH_2CH_3 \qquad (10)$$

$$CH_3CH_2CH_2\cdot + CH_3CH_2CH_3 \longrightarrow CH_3CH_2CH_3 + CH_3\dot{C}HCH_3 \qquad (11)$$

The only experimental evidence of the existence of any of these steps would be the occurrence of *n*-hexane in the reaction products. These reactions however are unlikely to occur to any large extent.

The rate of formation of *n*-propyl chloride can be written as

$$\frac{d(CH_3CH_2CH_2Cl)}{dt} = R_{CH_3CH_2CH_2Cl} = k_{3a}[CH_3CH_2CH_2\cdot][Cl_2] \qquad (12)$$

Dividing this expression by (8) and neglecting reactions (9), (10) and (11) we obtain

$$\frac{R_{CH_3CH_2CH_2Cl}}{R_{CH_3\cdot(C_2H_4)}} = \frac{k_{3a}[CH_3CH_2CH_2\cdot][Cl_2]}{k_4[CH_3CH_2CH_2\cdot]}$$

$$= \frac{k_{3a}}{k_4}\ [Cl_2] \qquad (13)$$

Assuming the amount of reaction is small we can write

$$R_{CH_3\cdot(C_2H_4)} \simeq [CH_3Cl]\ /t \qquad (14)$$

and $$R_{CH_3CH_2CH_2Cl} \simeq [CH_3CH_2CH_2Cl]\ /t \qquad (15)$$

Therefore

$$\frac{k_{3a}}{k_4} = \frac{[CH_3CH_2CH_2Cl]}{[CH_3Cl][Cl_2]} \qquad (16)$$

The concentration of chlorine is the initial concentration and for the above expression to be valid must not decrease significantly. This chlorine concentration can easily be measured as can the amounts of *n*-propyl chloride and methyl chloride produced. The rate constant for the decomposition of the *n*-propyl radical can therefore be found

if a value for the rate constant for the reaction of *n*-propyl radicals with molecular chlorine is known or can be estimated. Goldfinger and workers [32,34] calculated the rate parameters for the reaction of ethyl radicals with molecular chlorine and reported a value for the activation energy of 1 k cal and a value for log A of 10.1.

Another way of approaching the problem would be to use a steady-state treatment. Ignoring steps involving *sec*-propyl radicals we can write

$$0 = \frac{d[Cl\cdot]}{dt} = 2\,k_1[Cl_2][M] + k_{3a}[Pr\cdot][Cl_2] + k_5[Me\cdot][Cl_2] + k_7[ClCH_2CH_2\cdot][Cl_2] - k_{2a}[Cl\cdot][PrH] - 2k_{-1}[Cl\cdot]^2[M] - k_6[Cl\cdot][C_2H_4] \quad (17)$$

$$0 = \frac{d[Pr\cdot]}{dt} = k_{2a}[Cl\cdot][PrH] - k_{3a}[Pr\cdot][Cl_2] - k_4[Pr\cdot] \quad (18)$$

$$0 = \frac{d[Me\cdot]}{dt} = k_4[Pr\cdot] - k_5[Me\cdot][Cl_2] \quad (19)$$

$$0 = \frac{d[ClCH_2CH_2\cdot]}{dt} = k_6[Cl\cdot][C_2H_4] - k_7[ClCH_2CH_2\cdot][Cl_2] \quad (20)$$

Adding (17) ⟶ (20) we obtain

$$2\ k_1[Cl_2][M] = 2\ k_{-1}[Cl\cdot]^2[M]$$

$$[Cl\cdot]^2 = \frac{k_1}{k_{-1}}\ [Cl_2]$$

but $K_{eq} = k_1/k_{-1}$

therefore $[Cl\cdot]^2 = K_{eq}[Cl_2]$ (21)

$$R_{Me\cdot(MeCl)} = k_4[Pr\cdot]$$

from (18)

$$[Pr\cdot] = \frac{k_{2a}[PrH][Cl\cdot]}{k_{3a}[Cl_2] + k_4}$$

therefore

$$R_{MeCl} = \frac{k_4\ k_{2a}[PrH]\ K_{eq}^{\frac{1}{2}}[Cl_2]^{\frac{1}{2}}}{k_{3a}[Cl_2] + k_4} \qquad (22)$$

As for the previous expression (16), k_{3a} has to be estimated. In this case however k_{2a} also has to be found. For *n*-propyl radicals this value is known [33]. It should therefore be possible to find k_{2a} for any other radical using a competitive technique with propane.

This can be seen by the following reaction scheme

$$Cl_2 + M \longrightarrow 2Cl\cdot + M$$

$$n\text{-}PrH + Cl\cdot \xrightarrow{k_{2a}} n\text{-}Pr\cdot + HCl$$

$$n\text{-}R'H + Cl\cdot \xrightarrow{k'_{2a}} n\text{-}R'\cdot + HCl$$

$$n\text{-}Pr\cdot + Cl_2 \xrightarrow{k_{3a}} n\text{-}PrCl + Cl\cdot$$

$$n\text{-}R'\cdot + Cl_2 \xrightarrow{k'_{3a}} n\text{-}R'Cl + Cl\cdot$$

If this reaction is carried out at low temperatures, generating chlorine atoms photolytically, the only fate of the radicals is reaction with molecular chlorine to form the two chlorides. We can therefore write

$$\frac{d[n\text{-}Pr\cdot]}{dt} = k_{2a}[PrH][Cl\cdot] \qquad (23)$$

$$\frac{d[n\text{-}R'\cdot]}{dt} = k'_{2a}[R'H][Cl\cdot] \qquad (24)$$

k_{2a}/k'_{2a} can now be evaluated by the same method as described by Knox and Nelson [33].

Dividing (23) by (24)

$$\frac{d[n\text{-Pr}\cdot]/dt}{d[n\text{-R}'\cdot]/dt} = \frac{k_{2a}[PrH]}{k'_{2a}[R'H]} \tag{25}$$

Integration between the initial and final concentrations of PrH and R'H gives

$$\frac{k_{2a}}{k'_{2a}} = \frac{\ln([PrH]_i/[PrH]_f)}{\ln([R'H]_i/[R'H]_f)} \tag{26}$$

where i and f are the initial and final concentrations.

Writing $\Delta PrH = [PrH]_i - [PrH]_f$

and $\Delta R'H = [R'H]_i - [R'H]_f$

$$\frac{k_{2a}}{k'_{2a}} = \frac{\ln(1 + \Delta PrH/[PrH]_f)}{\ln(1 + \Delta R'H/[R'H]_f)}$$

If the extent of reaction is small then the approximation

$$\ln(1 + \Delta PrH/[PrH]_f) \simeq \Delta PrH/[PrH]_i$$

as $\Delta PrH/[PrH]_f \longrightarrow 0$, can be made and similarly for R'H.

Equation (26) now becomes

$$\frac{k_{2a}}{k'_{2a}} = \frac{\Delta PrH[R'H]_i}{\Delta R'H[PrH]_i} \tag{27}$$

as the change in hydrocarbon concentration equals the amount of chloride formed (27) can be written

$$\frac{k_{2a}}{k'_{2a}} = \frac{[n\text{-PrCl}]_f}{[n\text{-R'Cl}]_f} \times \frac{[R'H]_i}{[PrH]_i} \qquad (28)$$

Because k_{2a} for propane is important in obtaining the value for all other halopropanes the value was checked relative to k_{2b} as in previous work [33].

The Arrhenius equation can be written

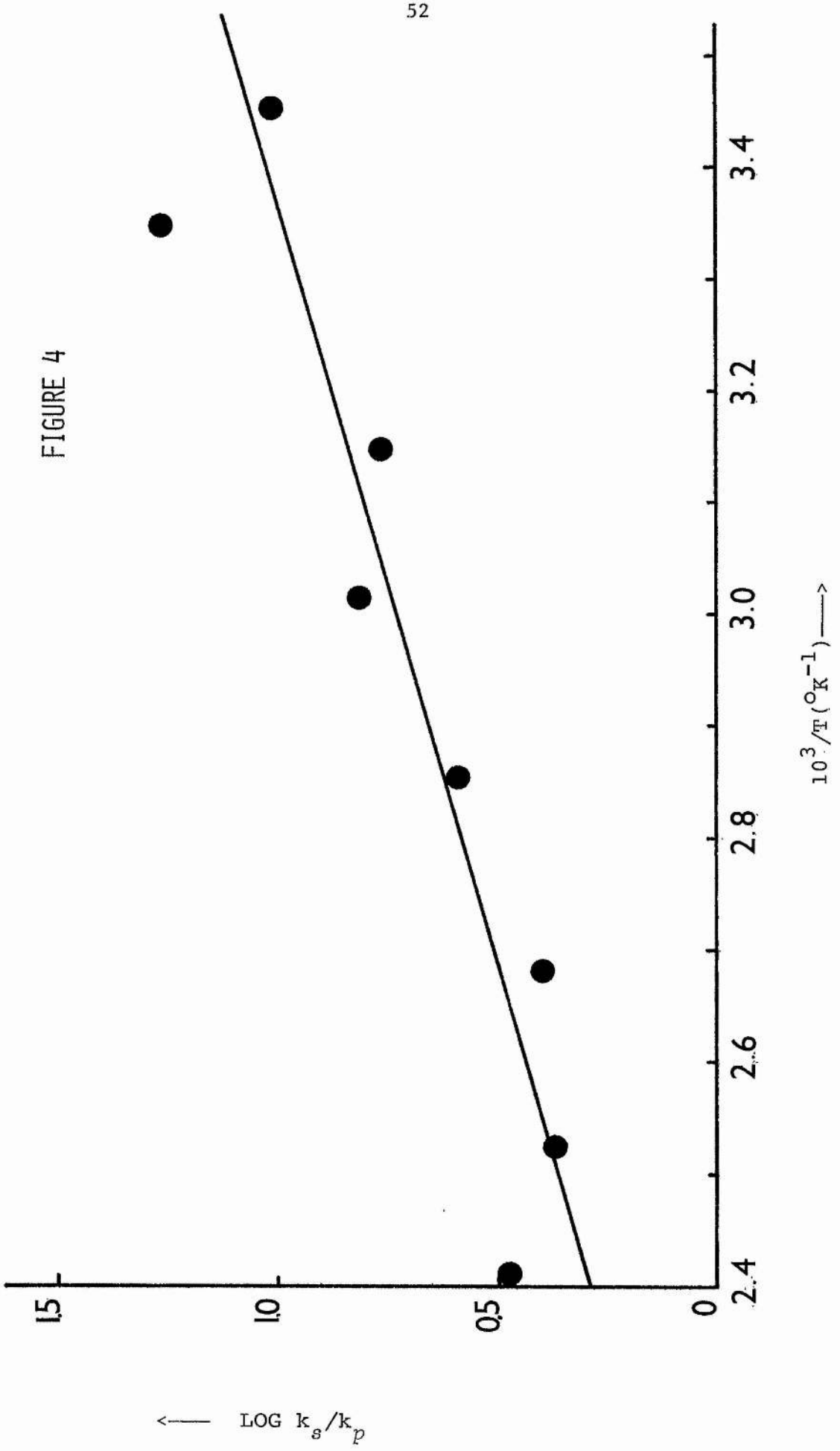
$$\log k = \log A - \frac{E}{2.303RT}$$

For competitive runs this becomes

$$\log \frac{k}{k'} = \log \frac{A}{A'} - \frac{(E - E')}{2.303RT}$$

The results obtained are given in Table 1/2 and the Arrhenius plot for the result (figure 4) gives a straight line very similar to that obtained by Knox. The difference in activation energies between the normal and secondary hydrogens ($E_p - E_s$) is 329 cals. compared with a value of 320 cals. obtained by Knox. The errors for this work are large in comparison with the activation energy and as seen from the Arrhenius plot there is a large scatter of points. However this work was carried out to check known values and this it has done satisfactorily. The difference in the value of log A_s/A_n to that compared with the work of Knox, although large, falls inside the limitsof experimental error.

FIGURE 4



The results were obtained using equation (28) in a modified form

$$\frac{k_{2a}}{k_{2b}} = \frac{[n\text{-PrCl}]_f}{[sec\text{-PrCl}]_f} \times \frac{[PrH]}{[PrH]}$$

$$\frac{k_{2a}}{k_{2b}} = \frac{[n\text{-PrCl}]_f}{[sec\text{-PrCl}]_f} \qquad (29)$$

This equation is valid at low temperatures where the only known fate of the propyl radicals is reaction with molecular chlorine.

Analysis of the products from the high temperature chlorination of propane indicated that the reaction schemes (1) → (7) was not correct. The conditions of analysis used were suitable for detecting even small amounts of methyl chloride and yet none was found in any of the experiments performed. Methane and ethane however were found and the reactions

$$M\cdot + 2CH_3\cdot \rightleftharpoons M + C_2H_6 \qquad (30)$$

$$CH_3\cdot + C_3H_8 \longrightarrow CH_4 + n\text{-}C_3H_7\cdot + sec\text{-}C_3H_7\cdot \qquad (31)$$

appear to be the only fate of the methyl radicals. This would be likely to cause great problems as instead of measuring the amount of methyl chloride formed after a certain time, equation (16) becomes

$$\frac{k_{3a}}{k_4} = \frac{[CH_3CH_2CH_2Cl]}{([CH_4] + 2[C_2H_6])[Cl_2]} \qquad (32)$$

As previously mentioned, great problems arose in the quantitative measurement of methane as it will not completely condense at liquid nitrogen temperature.

One possibility not considered yet is the measurement of ethylene and 1,2-dichloroethane formed. Analysis did not show any presence of 1,2-dichloroethane in any of the runs carried out. In fact no products which could have originated from ethylene were identified and it was therefore presumed that the amount of ethylene measured accounted for all the ethylene resulting from the decomposition of *n*-propyl radicals. The expressions giving the rate constant for the *n*-propyl radical decomposition therefore takes the form

$$\frac{k_{3a}}{k_4} = \frac{[CH_3CH_2CH_2Cl]}{[C_2H_4]\,[Cl_2]} \tag{33}$$

or

$$R_{(C_2H_4)} = k_4 \frac{k_{2a}[PrH]\,K_{eq}^{\frac{1}{2}}[Cl_2]^{\frac{1}{2}}}{k_{3a}[Cl_2] + k_4} \tag{34}$$

One of the major products identified was propylene produced by the thermal decomposition of the propyl chlorides.

$$CH_3CH_2CH_2Cl \longrightarrow CH_3CH{=}CH_2 + HCl \tag{35}$$

$$CH_3CHClCH_3 \longrightarrow CH_3CH{=}CH_2 + HCl \tag{36}$$

A rate constant equation for the dehydrochlorination of *n*-propyl chloride

$$\log k = 13.45 - 55000/2.303RT \ (sec^{-1})$$

is given by Barton, Head and Williams [35] and for *sec*-propyl chloride Barton and Head [36] give the expression

$$\log k = 13.4 - 50500/2.303RT \ (sec^{-1})$$

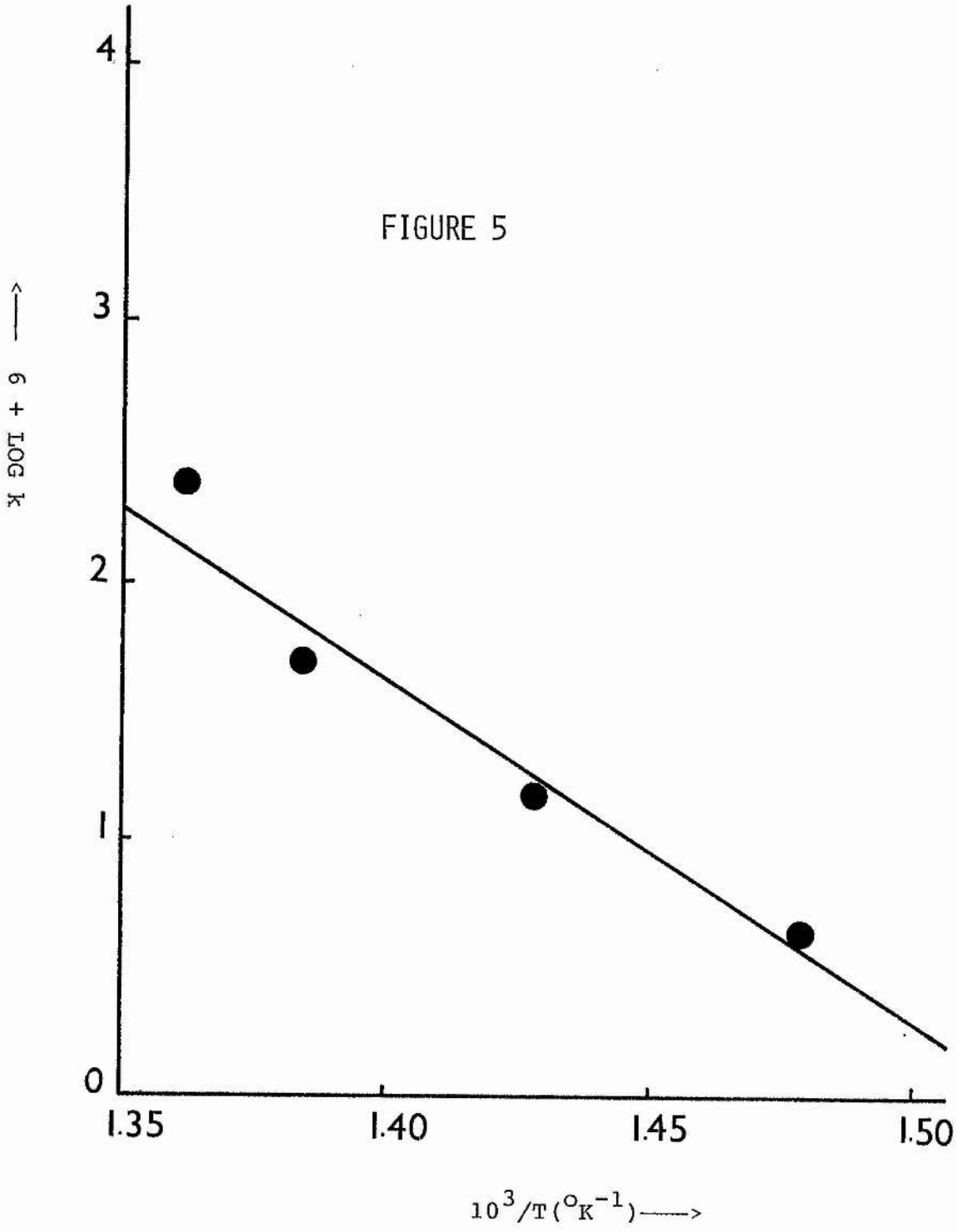
It is therefore most likely that the propylene formed originates from the dehydrochlorination of the *sec*-propyl chloride particularly at the lower temperatures due to the difference in activation energies of 4.5 kcals $mols^{-1}$.

The results obtained from the high temperature chlorination of propane suggested that some of the *n*-propyl chloride was breaking down in the experiments carried out in the higher temperature range. A study of the decomposition of the propyl chlorides was therefore carried out using the same apparatus used in the high temperature chlorination of propane.

The results obtained are given in Tables 1/3 and 1/4 and the graphs plotted in Figures 5 → 9. From the results obtained from a least squares plot for *n*-propyl chloride (Figure 5) we derive the expression

$$\log k \ (sec^{-1}) = 13.95 \ (\pm 1.10) - 59950 \ (\pm 7140)/2.303RT$$

FIGURE 5



From the results obtained from a least squares plot for *sec*-propyl chloride (Figure 6) we derive the expression

$$\log k\ (sec^{-1}) = 4.28\ (\pm\ 0.78) - 19670\ (\pm\ 5630)/2.303RT$$

The results for *n*-propyl chloride decomposition agree most favourably with the previous work. There is a high experimental error due to the small number of runs carried out but it must be remembered that the purpose of the exercise was to check that the same results were obtained with our apparatus.

The expression obtained from the *sec*-propyl chloride results is clearly incorrect. It is obvious from the plot (Figure 6) that the points form a curve and therefore a simple unimolecular decomposition is not taking place. Swinbourne [37] states that the decomposition of a particular class of chlorinated hydrocarbons, of which *sec*-propyl chloride is one, exhibit first-order kinetics, with no apparent induction period, when carried out in 'seasoned' reaction vessels. The work was carried out in a new reaction vessel and no attempt had been made to 'season' it.

In both experiments k was calculated using the expression

$$k = \frac{2.303}{t} \log \frac{[PrCl] + [Propene]}{[PrCl]} \qquad (37)$$

The most useful information for our purpose is contained in Figures 8 and 9. It can be seen from these plots that under the conditions used in the particular apparatus there is very little decomposition of *n*-propyl chloride below a value of $10^3/T = 1.45$ (i.e. $420^{\circ}C$). *sec*-Propyl chloride however decomposes to a considerable extent above $10^3/T = 1.60$ (i.e. $350^{\circ}C$).

FIGURE 6

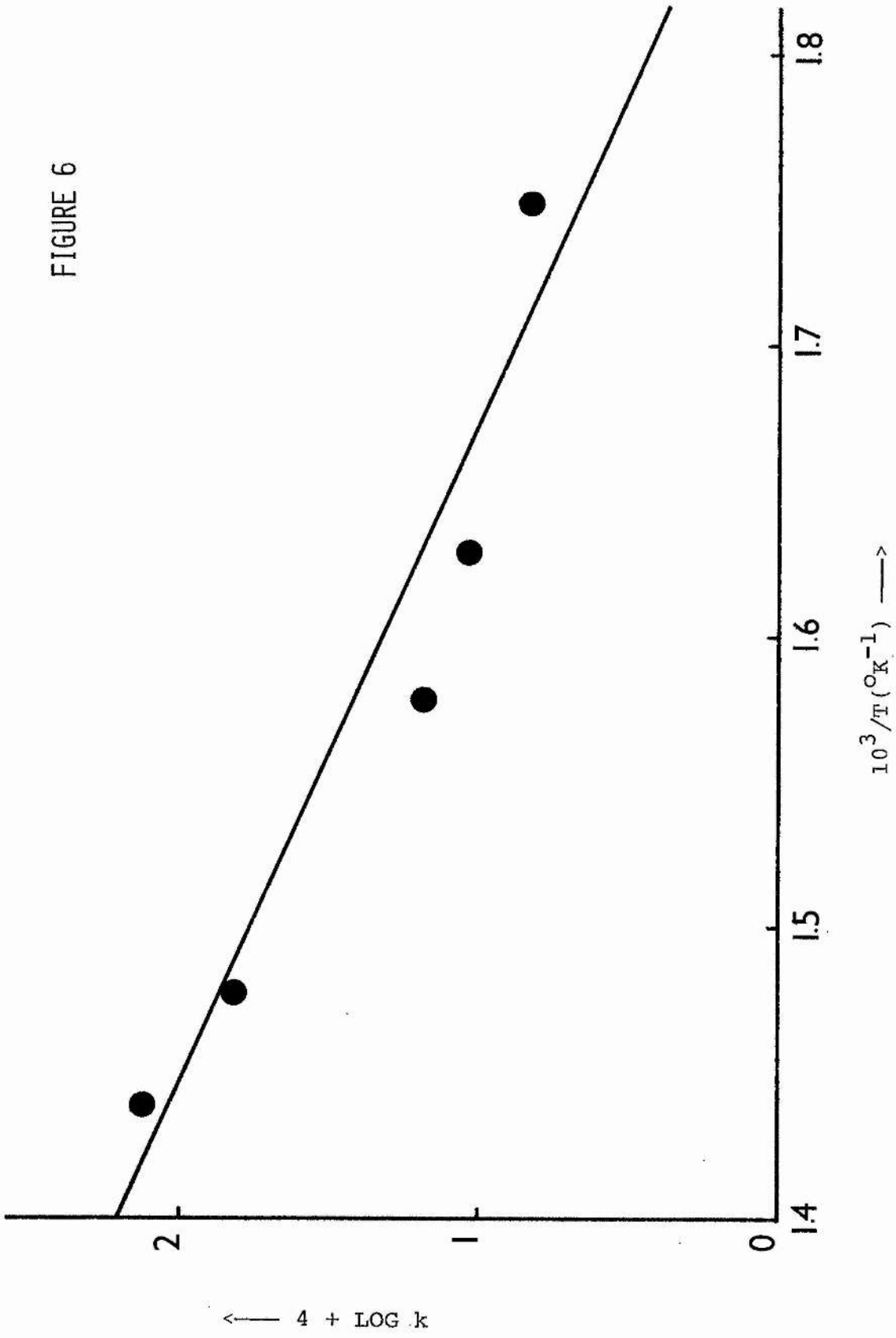
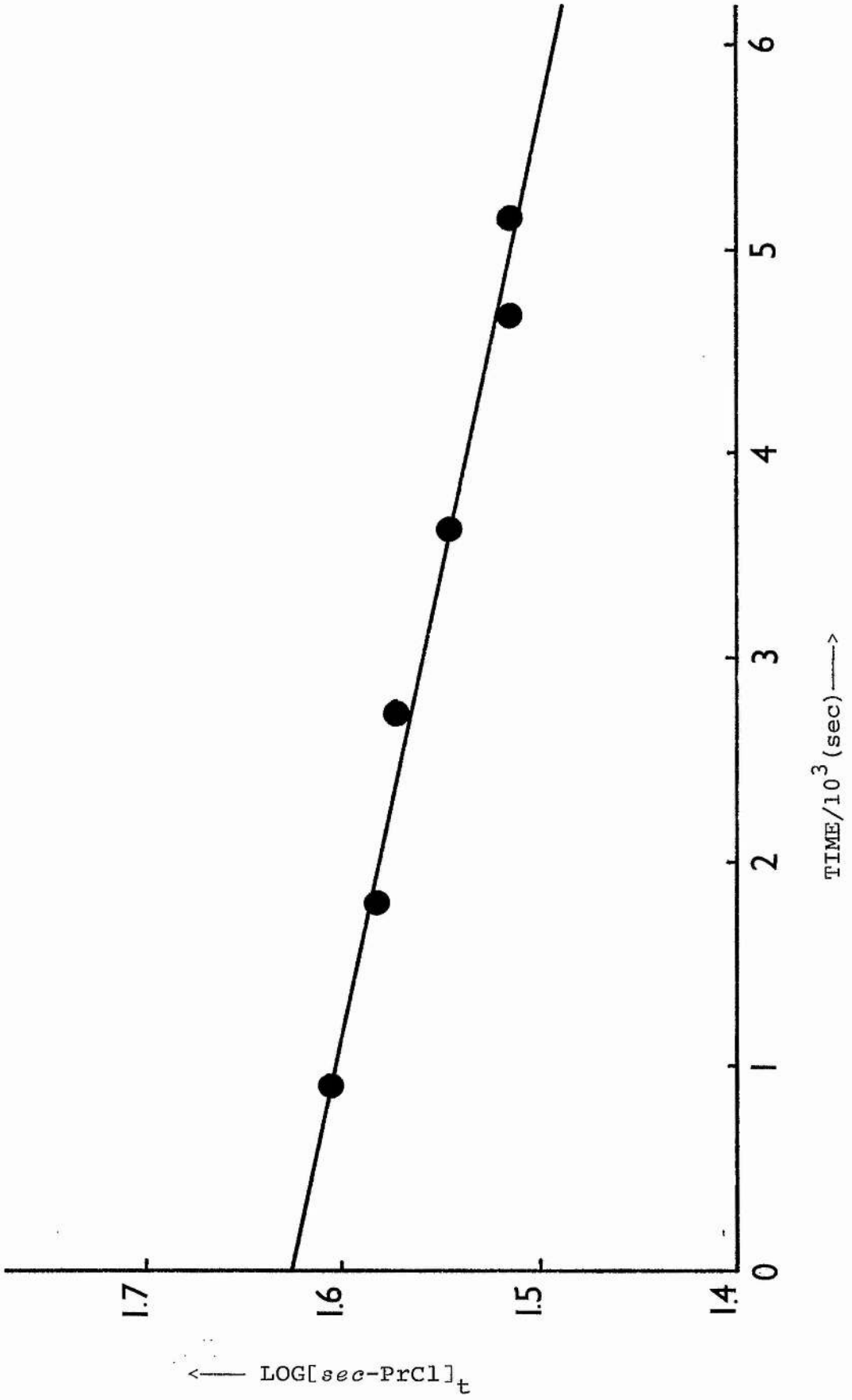


FIGURE 7



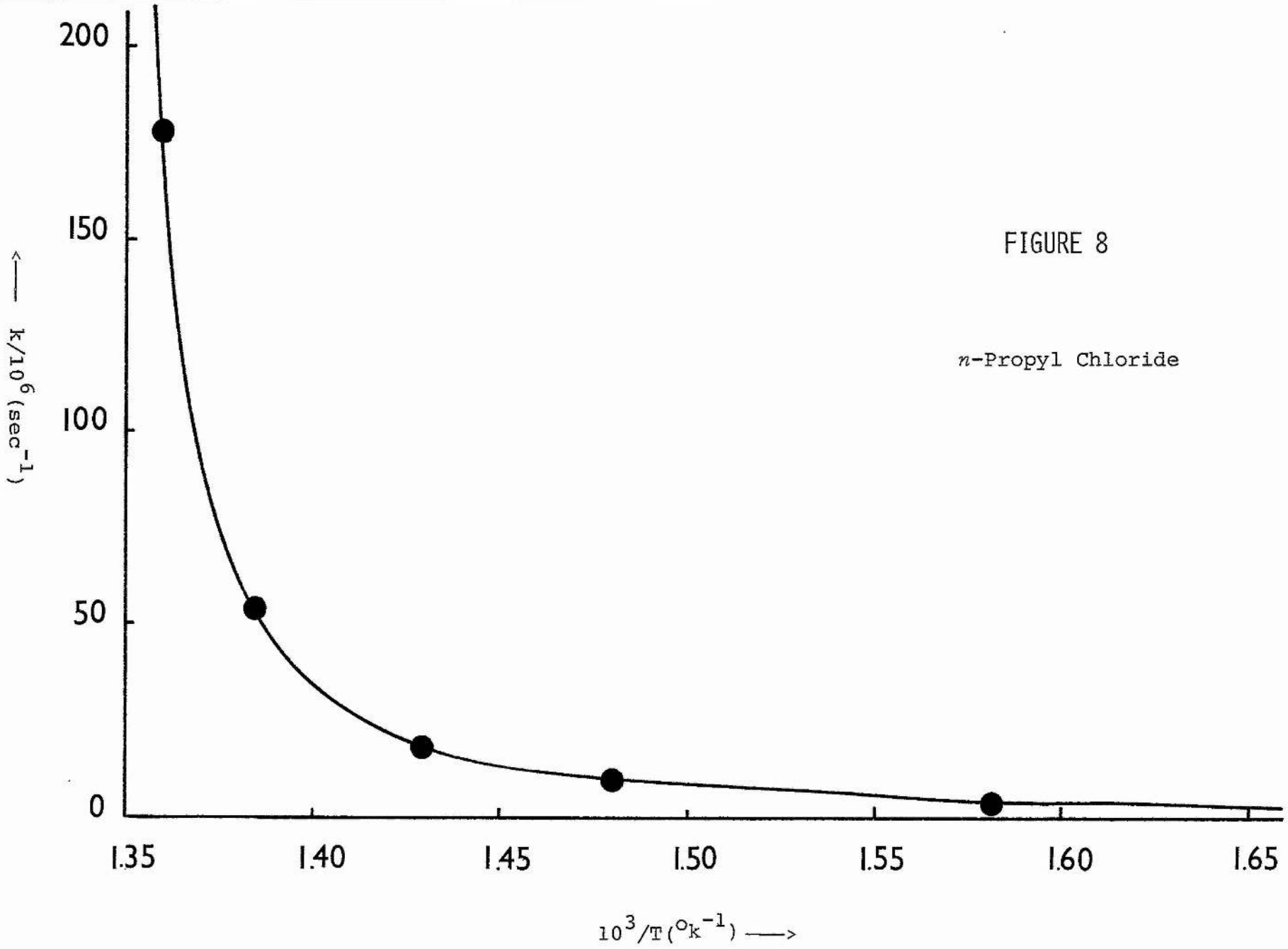
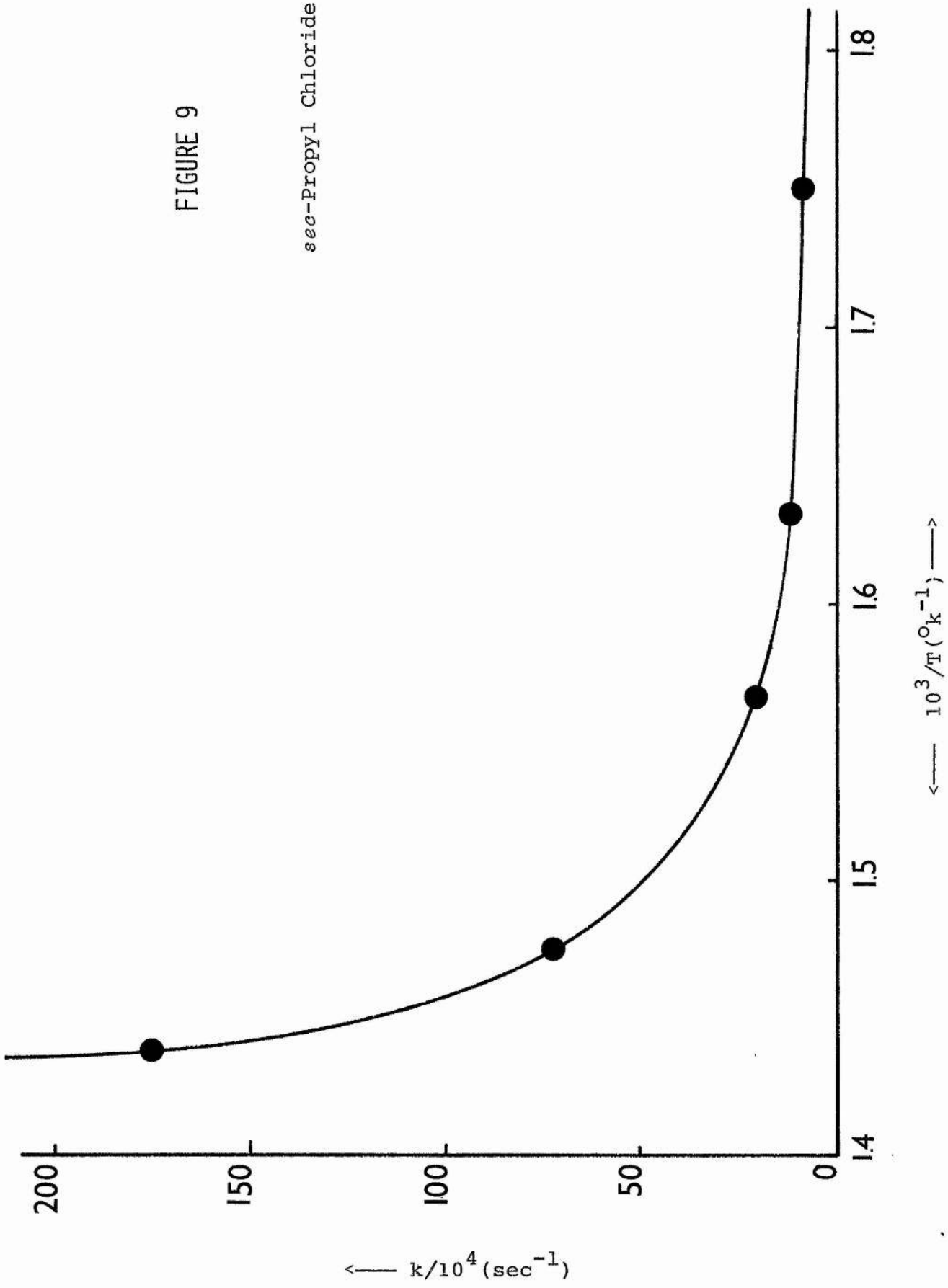


FIGURE 8

n-Propyl Chloride

FIGURE 9

sec-Propyl Chloride



A basic assumption made before the start of experimental work on the high temperature chlorination of propane, or indeed any other compound, was that there was no significant reduction in chlorine concentration during the course of the reaction. It became increasingly obvious however that the reaction was extremely rapid and that all the chlorine was used up in a very short time. Very short reaction times could not be adopted because the design of the apparatus did not allow the reactants to reach the required temperature quickly enough.

If we assume that the chlorine concentration does not change significantly, a plot of the results obtained (Table 1/5, Figure 10) should enable us to find a value for the Arrhenius parameters for the decomposition of *n*-propyl radicals. The plot obtained was a straight line and a least squares calculation of the results enabled us to obtain a value for the differences in activation energy $E_4 - E_{3a}$ of 27.1 ($\pm$ 4.6) kcals. E_{3a} has an estimated value of 1 kcals [32,34]. If our assumptions were correct we would have a value for the activation energy for the decomposition of *n*-propyl radicals of 26.1 ($\pm$ 4.6) kcals. From the least squares calculation we also obtained a value for the intercept with the y-axis of -3.26 ($\pm$ 0.65). Again if our assumptions were correct this would give an approximate value for $\log A_{3a}/A_4$ of -3.26. $\log A_{3a}$ has an estimated value of 10.1 sec^{-1} thus giving a value for $\log A_4$ of 13.4 sec^{-1}. These results for the Arrhenius parameters agree very favourably with the results from previous work [23-28]. The most recent value for the rate expression has been obtained by Papic and Laidler [28] and is

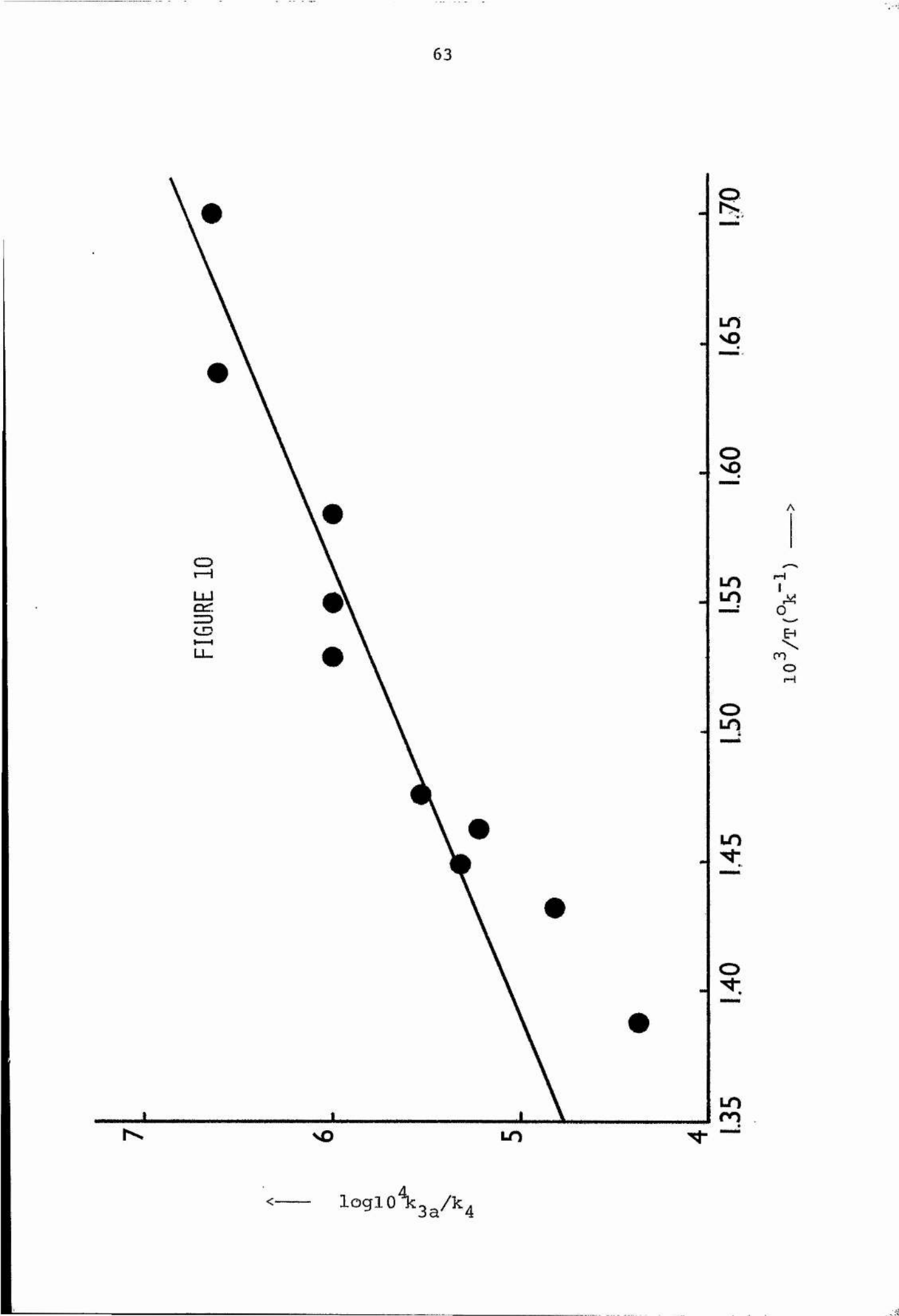


FIGURE 10
7
6
5
4
1.35
1.40
1.45
1.50
1.55
1.60
1.65
1.70
$\log 10^4 k_{3a}/k_4$ ⟵
$10^3/T(^oK^{-1})$ ⟶

$$\log k\ (sec^{-1}) = 14.40 - 32600/2.303RT$$

compared with our approximate value of

$$\log k\ (sec^{-1}) = 13.4\ (\pm\ 0.65) - 26100\ (\pm\ 4600)/2.303RT$$

At 400°C this gives a value of log k equal to 4.9 sec^{-1} compared with log k = 3.8 sec^{-1} using Laidler's expression at the same temperature.

Some experiments were carried out using bromine instead of chlorine. However the rate of reaction was still much too high and no advantage could be gained from its use.

The need for the reaction to proceed without a significant change in the chlorine concentration could only be eliminated by the adoption of competitive techniques.

The established parameters for the decomposition of *n*-propyl radicals could thereby be compared with the parameters for the decomposition of halopropyl radicals.

The first experiments were performed with 2,2-difluoropropane. This was considered the most suitable fluoropropane to study first because it was thought most unlikely to eliminate hydrogen fluoride at the temperatures used. We can amend the reaction scheme (1) → (4) to give the following

$$Cl_2 + M \rightleftharpoons 2Cl\cdot + M \qquad (1)$$

$$Cl\cdot + CH_3CH_2CH_3 \longrightarrow CH_3CH_2CH_2\cdot + HCl \qquad (2a)$$

$$Cl\cdot + CH_3CF_2CH_3 \longrightarrow CH_3CF_2CH_2\cdot + HCl \qquad (2')$$

$$CH_3CH_2CH_2\cdot + Cl_2 \longrightarrow CH_3CH_2CH_2Cl + Cl\cdot \qquad (3a)$$

$$CH_3CF_2CH_2\cdot + Cl_2 \longrightarrow CH_3CF_2CH_2Cl + Cl\cdot \qquad (3')$$

$$CH_3CH_2CH_2\cdot \longrightarrow CH_3\cdot + CH_2{=}CH_2 \qquad (4)$$

$$CH_3CF_2CH_2\cdot \longrightarrow CH_3\cdot + CF_2{=}CH_2 \qquad (4')$$

$$R_{CH_2=CH_2} = k_4[CH_3CH_2CH_2\cdot]$$

$$R_{CF_2=CH_2} = k_4'[CH_3CF_2CH_2\cdot]$$

$$R_{CH_3CH_2CH_2Cl} = k_{3a}[Cl_2][CH_3CH_2CH_2\cdot]$$

$$R_{CH_3CF_2CH_2Cl} = k_{3a}'[Cl_2][CH_3CF_2CH_2\cdot]$$

If the amount of reaction is small we can write

$$\frac{[CH_2=CH_2]_f[CH_3CF_2CH_2Cl]_f}{[CF_2=CH_2]_f[CH_3CH_2CH_2Cl]_f} = \frac{k_4\ k_3'}{k_4'\ k_{3a}} \qquad (38)$$

k_3 and k_{3a}' cannot be determined easily although they will both have activation energies of < 2 kcal mol^{-1}. k_4 (known) and k_4' will

have activation energies around 30 kcal mol^{-1}. Therefore a plot of the left-hand side of (38) against $10^3/RT$ will give a good estimate of $E_4' - E_4$ and hence a value for the activation energy for the thermal decomposition of the 2,2-difluoropropyl radical.

An alternative method of obtaining a value for k_4' is possible. As in the case of propane we can write

$$\frac{d[CH_3CH_2CH_2\cdot]}{dt} = 0 = k_{2a}[CH_3CH_2CH_3][Cl\cdot] - k_{3a}[CH_3CH_2CH_2\cdot][Cl_2] - k_4[CH_3CH_2CH_2\cdot]$$

$$\frac{d[CH_3CF_2CH_2\cdot]}{dt} = 0 = k_2'[CH_3CF_2CH_3][Cl\cdot] - k_3'[CH_3CF_2CH_2\cdot][Cl_2] - k_4'[CH_3CF_2CH_2\cdot]$$

therefore

$$[CH_3CH_2CH_2\cdot] = \frac{k_{2a}[CH_3CH_2CH_3][Cl\cdot]}{k_{3a}[Cl_2] - k_4}$$

and

$$[CH_3CF_2CH_2\cdot] = \frac{k_2'[CH_3CF_2CH_3][Cl\cdot]}{k_3'[Cl_2] - k_4'}$$

$$R_{CH_2=CH_2} = k_4[CH_3CH_2CH_2\cdot]$$

$$R_{CF_2=CH_2} = k_4'[CH_3CF_2CH_2\cdot]$$

hence

$$\frac{R_{CH_2=CH_2}}{R_{CF_2=CH_2}} = \frac{k_{2a}[CH_3CH_2CH_3]}{k_2'[CH_3CF_2CH_3]} \quad \frac{(k_3'/k_4' + 1)}{(k_{3a}/k_4 + 1)}$$

k_3' and k_3 again have to be estimated. The ratio k_{2a}/k_2' can be found by the low temperature competitive photolytic chlorination of propane and 2,2-difluoropropane.

Equation (28) can be amended to

$$\frac{k_{2a}}{k_2'} = \frac{[CH_3CH_2CH_2Cl]_f[CH_3CF_2CH_3]_i}{[CH_3CF_2CH_2Cl]_f[CH_3CH_2CH_3]_i} \qquad (39)$$

A constant ratio of reactants was used in these photolytic runs and equation (39) becomes

$$\frac{k_{2a}}{k_2'} = \frac{[CH_3CH_2CH_2Cl]_f}{[CH_3CF_2CH_2Cl]_f} \times 30.62 \qquad (40)$$

An Arrhenius plot of the results of these experiments (Table 1/6, Figure 11) gave a straight line with a gradient of 0.841 ($\pm$ 0.277) and intercept of the y-axis 0.636 ($\pm$ 0.116). This gives a value for the difference in activation energy of $E_2' - E_{2a}$ = 3.848 kcals mol^{-1}. E_{2a} has a reported value [33] of 1 kcal mol^{-1} therefore the activation energy E_2' = 4.848 kcal mol^{-1}. The intercept on the y-axis = log A_{2a}/A_2'. Taking the value of log A_{2a} [33] as 10.2 dm^3 mol^{-1} sec^{-1} we arrive at a value for log A_2' of 10.8 dm^3 mol^{-1} sec^{-1}.

The value of 4.848 kcal mol^{-1} seems very high for hydrogen abstraction by chlorine. Henne [38,39,40] has carried out a number of

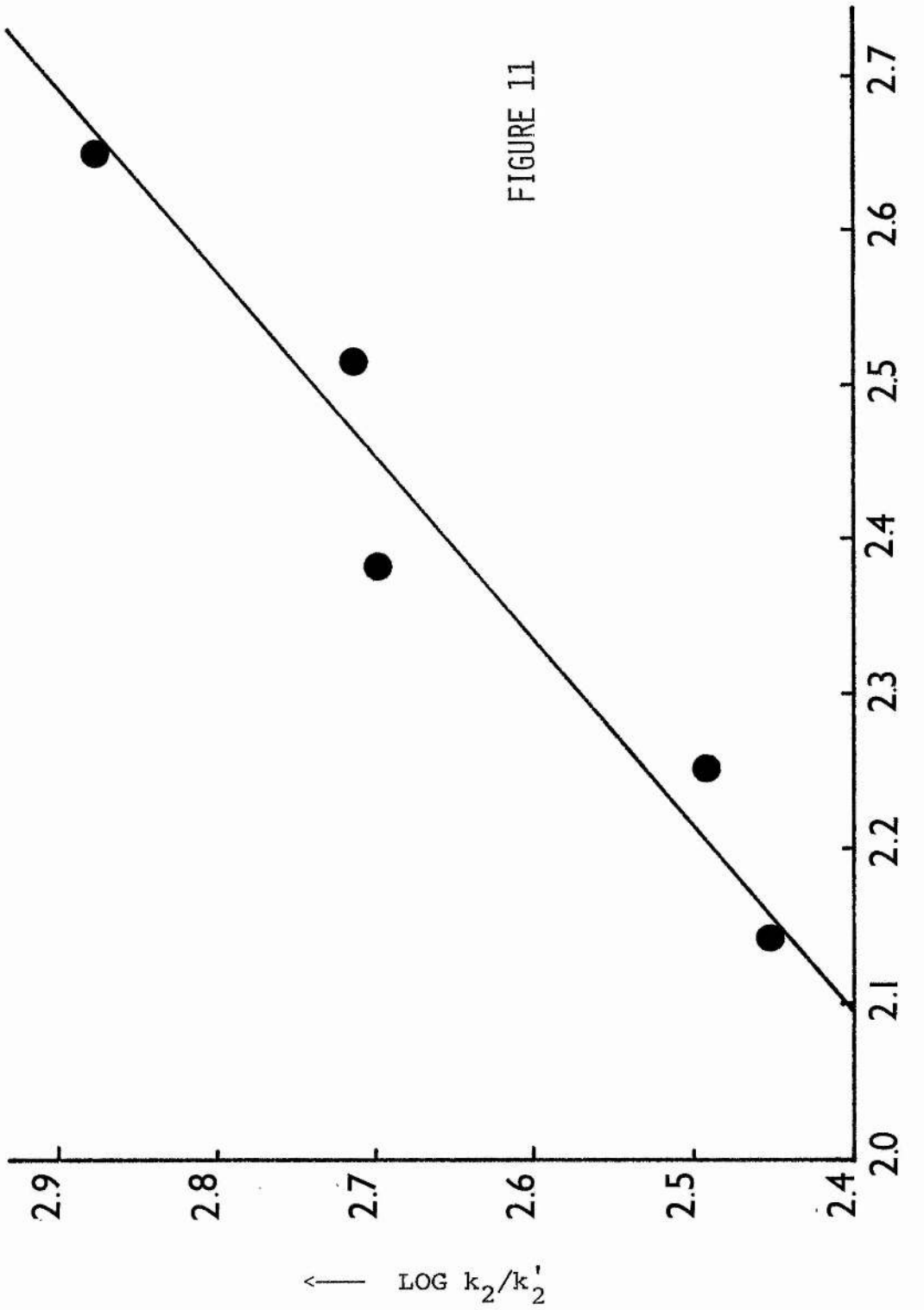


FIGURE 11

studies on the directive effects of fluorine substituted into alkanes to hydrogen abstraction by chlorine. On studying 2,2-difluorobutane he found that chlorination was directed away from the alpha methyl group and further chlorination tended to accumulate chlorine atoms on the same carbon atoms. Martens [41] reports a value for the activation energy for chlorination of 1,1-difluoroethane, in the primary position, of 5.405 kcal mol^{-1}. This is in excellent agreement with our value for 2,2-difluoropropane. The deactivation of the primary hydrogens to chlorination can only be due to the very strong inductive effect of the β-fluorine atoms.

Before competitive runs with propane were carried out at high temperatures, chlorination of 2,2-difluoropropane alone was carried out so as to be able to identify products of this reaction. The first run was carried out at 395°C under similar conditions to those used for the high temperature chlorination of propane. A large peak appeared (approximately 30% the size of the reactant peak area) which eluted immediately before the reactant.

A run was carried out with no chlorine present and the same peak still occurred. On analysis using mass spectrometry the unknown peak was identified as 2-fluoropropene. This had almost certainly been formed by the elimination of hydrogen fluoride from the starting material. It was therefore not possible to carry out the intended reactions due to the rapid decomposition of the starting material.

PART II

A Study of some Aliphatic Radical Transfer Reactions

INTRODUCTION

Radical transfer reactions are reactions in which the free radical abstracts an atom from another molecule thereby producing a new radical.

$$A{-}B + X^{\cdot} \longrightarrow X{-}A + B^{\cdot}$$

In the case of saturated aliphatic compounds the atom abstracted is nearly always a hydrogen atom.

$$R{-}H + X^{\cdot} \longrightarrow R^{\cdot} + H{-}X$$

The new radical in turn may abstract an atom from another molecule thus leading to a chain reaction.

The ease of abstraction of hydrogen atoms by all free radicals is known to follow the order *tertiary* > *secondary* > *primary*. There is however a considerable variation in the selectivity of individual radicals. The introduction of a substituent into an alkane can have a very pronounced effect on the reactivity of the alkane. This depends on the nature of the attacking radical the reactivity of which may be accelerated or retarded depending upon the substituent and the position of attack.

The factors involved in free radical hydrogen abstraction are discussed by Tedder [42] in terms of potential energy surfaces in a manner originally developed by Evans and Polanyi [43]. This approach shows that the activation energy for the abstraction process is controlled by four factors: The strength of the radical-hydrogen

bond formed, the strength of the aliphatic hydrogen bond broken, the repulsion between the aliphatic radical formed and the new molecule, the repulsion between the attacking radical and the aliphatic compound.

The first factor is of great importance in the determination of the activation energy of hydrogen abstraction although there is no linear relationship between D(H-X) and the activation energy. In the reaction of fluorine with ethane the activation energy for the hydrogen abstraction process is 0.2 kcal mol^{-1} and the strength of the H-F bond formed is given by D(H-F) = 136 kcal mol^{-1} [44]. In the bromination of ethane however the activation energy for hydrogen abstraction is 13.3 kcal mol^{-1} and the bond strength is D(H-Br) = 87 kcal mol^{-1} [45].

The importance of the second factor is illustrated by the relative ease of abstraction of tertiary, secondary and primary hydrogen atoms. There exists a linear relationship between the activation energy of hydrogen abstraction and the strength of the broken bond for methyl radicals with alkanes [46]. A more general relationship between the activation energy and the heat of reaction (i.e. the strength of the broken bond) was proposed by Evans and Polanyi [43]. The relationship

$$E = \alpha\Delta H + C \quad (\text{where } 0 < \alpha < 1 \text{ and } \alpha \text{ and } C \text{ are constants})$$

is known as the Evans-Polanyi equation and holds for a particular aliphatic compound or a particular radical provided there is no variation in polar effects present. α is generally larger for

reactions with greater activation energies e.g. bromine has a value of $\alpha = 0.86$ whereas methyl radicals have a value of $\alpha = 0.49$[47].

The repulsive forces controlling the activation energies of hydrogen abstraction are Coulombic, due to electronic displacements in the reacting molecule, caused by substituents in the molecule. In the third factor, repulsion between the new radical and the new molecule, substituents will have no effect on abstraction by methyl radicals or hydrogen atoms as the product molecule is non-polar. Halogenation however will produce the highly-polar hydrogen halides and this factor will therefore have a major effect on the reactions with polar substituted aliphatic compounds. This polar effect is sometimes in opposition to a mesomeric effect caused by resonance stabilisation of the incipient radical. An example of this effect is in the chlorination of methane. There is a reduction in activation energy for the abstraction of the second hydrogen atom (i.e. abstraction from methyl chloride). The activation energy rises again for the chlorination of methylene chloride and chloroform. The same effect occurs for methyl radicals also. In this case the deactivation due to polar effects does not exist and therefore any fall in activation energy is a measure of the resonance stabilisation of the incipient radical. This is in fact backed up by a proportionately larger decrease in the activation energy for methyl radicals.

For the fourth factor to be important, the attacking radical itself must have overall polarity. This effect is therefore unimportant when dealing with atomic species. An example of this

effect given by Tedder [42] is the hydrogen abstraction from ethane by trifluoromethyl radicals, hydrogen atoms and methyl radicals. The heat of reactions are very similar and yet the activation energies are 7.5, 8.7 and 11.2 kcals mol^{-1}. Obviously there are no polar effects due to the ethane or hydrogen atoms. Polar effects between trifluoromethyl radicals and ethane are attractive and repulsive in the case of methyl radicals thus causing the differences in activation energies.

The most extensive studies of hydrogen abstraction relate to halogenation. Chlorination being an important technical process has received much attention, much of the early work being carried out by Hass, McBee and Weber [48]. It was this group who introduced the much used concept of relative selectivity to describe the relative reactivities of different molecules or of different sites within a particular molecule. If there are x hydrogen atoms at position x in a molecule and y hydrogen atoms at position y, the relative selectivity per hydrogen atom can be written in the form:

$$RS_y^x = \frac{k_x}{k_y} \times \frac{y}{x}$$

k_x and k_y being the rates of hydrogen abstraction at that particular site.

Competitive methods for comparing relative rate constants between different molecules or at different sites within the same molecule are extensively used, utilising the direct analysis of reaction products. These can then be put on an absolute scale by doing competitive experiments with substrates for which the rate constant for hydrogen

abstraction is known. In the chlorination of alkanes for example, hydrogen can be added to the system as the rate constant for the reaction:

$$Cl\cdot + H_2 \longrightarrow H\cdot + HCl$$

is known [49]. This method has been used by Knox [33] to determine absolute Arrhenius parameters from relative Arrhenius parameters.

A method extensively used to determine absolute rate parameters is to find the rate constant for hydrogen abstraction relative to the rate constant for radical combination, the latter value is not only known for many radicals but is also considered to have a minimal activation energy which can be taken as zero.

The kinetics and mechanism of hydrogen abstraction by methyl radicals and trifluoromethyl radicals have been reviewed by Gray, Herod and Jones [50].

The work described in this section of the thesis is divided into two parts. The first part is concerned with the study of the reactions of trifluoromethyl radicals with butane and substituted butanes. The second part describes work carried out in a study of the reactions of methyl radicals with the same aliphatic compounds.

SECTION I

Hydrogen Abstraction Reactions of Trifluoromethyl Radicals

INTRODUCTION

The most commonly used sources of trifluoromethyl radicals have been photolytic. Trifluoroacetaldehyde [51], perfluoroacetic anhydride [52] and trifluoromethyl chloride [53] have been used although the most popular sources have been hexafluoroacetone, hexafluoroazomethane and trifluoromethyl iodide. Hexafluoroacetone has been the most extensively used source being both relatively cheap and readily available. It also has the advantage, as does hexafluoroazomethane, of providing an accurate monitor of the quantum yield of trifluoromethyl radicals by the direct measurement of carbon monoxide or nitrogen produced.

Trotmann-Dickenson and workers [54,55] used hexafluoroazomethane as a source of trifluoromethyl radicals in a study of hydrogen abstraction from a series of alkanes.

$$CF_3\cdot + RH \longrightarrow CF_3H + R^{\cdot} \qquad (1)$$

It was not possible to compare k_1 with the rate of trifluoromethyl radical combination because of a large amount of addition of trifluoromethyl radicals to the parent compound.

$$CF_3\cdot + CF_3N : NCF_3 \longrightarrow (CF_3)_2\dot{N}.NCF_3 \qquad (2)$$

$$(CF_3)_2\dot{N}.NCF_3 + CF_3\cdot \longrightarrow (CF_3)_2N.N(CF_3)_2 \qquad (3)$$

The rate constant k_1 was determined for the series of alkanes using a competitive technique. Deuterium was added to the system. The

rate constant k_1 was then compared with the rate constant for the reaction

$$CF_3\cdot + D_2 \longrightarrow CF_3D + D\cdot \qquad (4)$$

by measuring the relative amounts of production of fluoroform and deuteriofluoroform in a photolytic system containing the alkane, deuterium and hexafluoroazomethane. k_4 was previously known and therefore Arrhenius parameters could be calculated for reaction (1).

Ayscough, Polanyi and Steacie [56] studied the hydrogen transfer reactions of trifluoromethyl radicals with methane and ethane using hexafluoroacetone as the radical source. The only products found in these experiments were fluoroform, hexafluoroethane and carbon monoxide. They found no evidence for the trifluoromethyl radicals reacting with the radical source even at high temperatures.

The results obtained (6) agreed favourably with those obtained by Trotman-Dickenson (5). For hydrogen abstraction from ethane for example the results obtained by the two groups were

$$\log k = 8.63 - 7500/2.3RT \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1} \qquad (5)$$

$$\log k = 8.68 - 7500/2.3RT \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1} \qquad (6)$$

Part of a general study of the photolysis of trifluoroacetaldehyde by Dodd and Smith [51] involved hydrogen abstraction reactions by trifluoromethyl radicals from methane and isobutane. Kinetic studies

were complicated by the fact that the trifluoromethyl radicals also abstract hydrogen from the trifluoroacetaldehyde. The Arrhenius parameters obtained agreed favourably with results from other studies [56].

Alcock and Whittle [57] studied the reactions of trifluoromethyl radicals, generated from the photolysis of hexafluoroacetone, with methyl halides

$$CF_3\cdot + CH_3X \longrightarrow CF_3H + CH_2X\cdot \qquad (7a)$$

$$\longrightarrow CF_3X + CH_3\cdot \qquad (7b)$$

Arrhenius parameters for the reaction (7) were obtained where X equals hydrogen, chlorine, bromine and iodine. From the results the ease of abstraction of X was found to be in the order I > Br ~ H > Cl. In the case of iodine abstraction the reaction was extremely rapid and complicated side-reactions occurred. The activation energies for hydrogen abstraction by trifluoromethyl radicals from the methyl halides was found to be lower than the value for methane the value reducing in the order H > Cl > Br > I *.

Alcock and Whittle then went on to study the abstraction reactions of trifluoromethyl radicals with the series of chloromethanes first using hexafluoroacetone as a source [59], and later hexafluoroazomethane [60]. They found that the activation energy for hydrogen abstraction fell along the series CH_4 > CH_3Cl > CH_2Cl_2 > $CHCl_3$.

Cvetanovic, Raal and Steacie [61] showed in the analagous photolysis of acetone that complications arose from the photosensitized reactions

* The Cl and Br are reversed in order of low CH_3Br pressures.

involving the acetone. To establish whether or not this was happening with the hexafluoroacetone, the experiments were repeated using hexafluoroazomethane as a trifluoromethyl radical source. The results supported those previously obtained using hexafluoroacetone and therefore no evidence of photosensitized reactions existed.

Oksent'evich and Pravednikov [58] studied the hydrogen abstraction reactions of trifluoromethyl radicals, produced by the photolysis of hexafluoroacetone, with a series of fluoroethanes. A general trend of decreasing activation energies for hydrogen abstraction with increasing fluorination of the ethane was found. Unfortunately data for attack at one of the two specific sites within the fluoroethanes was not obtained. The results do show however that resonance stabilisation of the incipient fluoroalkyl radical plays an important role in the decreasing of the activation energies for hydrogen abstraction.

These results are in very poor agreement to those obtained by Giles, Quick and Whittle in a similar study [62]. They studied the reactions of trifluoromethyl radicals, produced by the photolysis of hexafluoroacetone, with fluoromethanes and fluoroethanes. With increased fluorination of methane, the activation energies for hydrogen abstraction by the trifluoromethyl radicals showed no measurable variation. The analogous case of increased chlorination of methane previously mentioned showed a decrease in activation energy for hydrogen abstraction. Whittle suggested that there is a direct cancelling out of the effect of the decrease in D(C-H) by the increase in polar effects.

In the case of hydrogen abstraction from fluoroethanes a large increase in activation energy was found in going from ethane to 1,1,1-trifluoroethane. This agreed favourably for previous studies of hydrogen abstraction from carbon atoms adjacent to carbon atoms containing fluorine [63]. For hydrogen abstraction from 1,1,2,2-tetrafluoroethane Whittle obtained an activation energy of 11.9 kcal mol^{-1}. There is no similarity to the value of 2.3 kcal mol^{-1} for the same reaction obtained by Oksent'erich.

Quick and Whittle extended the study of trifluoromethyl radical abstraction reactions to bromo- and fluoro-bromoethanes [65]. The hydrogen abstraction reactions of trifluoromethyl radicals in these halides were discussed fully along with the results obtained in past studies [59,60,62]. A conclusion was reached that ample evidence existed for the presence of polar effects in the reactions studied.

Morris and Thynne [64] used both hexafluoroacetone and trifluoromethyl iodide as photolytic sources of trifluoromethyl radicals to study hydrogen and deuterium abstraction from methanol and trideuteromethanol. To check their experimental and analytical technique they studied the reaction of *n*-butane with trifluoromethyl radicals using hexafluoroacetone and trifluoromethyl iodide. This reaction was chosen because it had been studied previously and Arrhenius parameters were known [56]. When trifluoromethyl iodide was used as a radical source, the values for the rate constant for hydrogen abstraction from *n*-butane were consistantly lower than those obtained when

hexafluoroacetone was the radical source. Examination of the reaction products of the runs where hexafluoroacetone was used showed the presence of butene-I and cis- and trans-butene-2 formed from the disproportionation of trifluoromethyl radicals and butyl radicals. This would account for the high values of the rate constant. When trifluoromethyl iodide was used however butene formation was inhibited since the butyl radicals could abstract iodine from trifluoromethyl iodide thus propagating the chain reaction.

Although the hydrogen abstraction reactions of trifluoromethyl radicals had received much attention no information existed on the attack by these radicals at specific sites within alkanes. Arican, Potter and Whytock [66] used trifluoromethyl iodide as a source of trifluoromethyl radicals to study their selectivity in hydrogen abstraction at specific sites in propane, *n*-butane and isobutane. This was possible because the alkyl radicals all formed alkyl iodides and product analysis of these gave a measurement of attack at each site.

The work described in this part of the thesis was carried out to discover what effects polar substituents have on the hydrogen abstraction reactions of trifluoromethyl radicals. Trifluoromethyl iodide was used as a radical source making it possible therefore to measure the selectivity at the different reaction sites in substituted butanes.

EXPERIMENTAL

MATERIALS

Trifluoromethyl Iodide (Bristol Organics) and *n*-butane (Matheson instrument grade) were both purified by trap to trap distillation, a middle fraction being taken in each case. Both gases were stored in glass bulbs, permanently attached to the vacuum line, with side-arms which could be surrounded by liquid nitrogen in order to freeze down the gases. The bulb containing trifluoromethyl iodide was surrounded by aluminium foil to protect it from daylight. The *n*-butane contained trace amounts of an impurity believed to be isobutane. The trifluoromethyl iodide contained small amounts of hexafluoroethane and iodine, produced by photodegradation.

n-Butyl chloride (Hopkin and Williams) was purified by the use of a Pye Unicam 105 preparative gas chromatograph to remove *sec*-butyl chloride. A 25% tritolyphosphate column (12') was used and two purifications were necessary to eliminate all the impurities. The *n*-butyl chloride was introduced onto the vacuum line and further purification by trap to trap distillation was carried out before it was stored in a glass finger.

Preparation of *n*-Butyl Fluoride [75,76]

Dimethylformamide (400ml) was redistilled and placed into a one litre, three neck, round bottomed flask containing anhydrous

potassium fluoride (116g). A stirrer, dropping funnel and four-step Vigreux column were fitted. The Vigreux column was fitted with a stillhead (with thermometer) and delivery tube to a cold finger which was immersed in a 'dry ice'/acetone mixture. The contents of the reaction flask were heated to 130°C with rapid stirring. *n*-Butyl bromide (100ml) was added to the reaction flask. The *n*-butyl fluoride was collected in the cold finger.

Purification was carried out in three stages using a Pye-Unicam 105 preparative gas chromatograph. The crude *n*-butyl fluoride contained some *n*-butyl bromide (approx 5%) and also some butene (approx 20%). The *n*-butyl bromide was first removed by the use of a 12', 25% squalane column at 100°C with a nitrogen carrier gas pressure of 20 psi. Separation of butene and *n*-butyl fluoride was poor at this temperature and only about 80% of the butene was removed. The second stage was carried out on the same column at 35°C and 20 psi pressure. This removed nearly all the butene and also traces of other light impurities. The final purification was carried out on a 12', 25% tritolylphosphate column at room temperature and a nitrogen carrier gas pressure of 8 psi.

The pure *n*-butyl fluoride was transferred to the vacuum line and further purification carried out by trap to trap distillation before being stored in a glass finger.

Preparation of 1,1,1-Trifluoropentane [29,30]

The reaction was carried out in a large stainless steel autoclave. Dry valeric acid (0.60 moles) was placed in the autoclave which was then cooled in a dry ice/acetone mixture to -80°C and the whole apparatus was evacuated using a rotary vacuum pump. Sulphur tetrafluoride (1.80 moles) was condensed into the autoclave and the valve for the whole assembly closed. The autoclave was then heated up to 140°C in an electric oven and a mechanical stirrer driven by an electro-magnetic device was employed. The reaction was carried out for 14 hours.

The autoclave was cooled to 0°C in an ice/water mixture. The gaseous products were then released through two glass washing bottles containing a solution of sodium hydroxide (57) to remove sulphur tetrafluoride, hydrogen fluoride and thionyl fluoride. The autoclave was then dismantled and toluene (200ml) was added. Excess sodium carbonate was added to neutralise any hydrogen fluoride present and the contents of the reaction chamber were transferred to a one litre round bottomed flask. A rough distillation was carried out, everything that came over below 95°C being collected.

Gas chromatography/Mass spectrometry revealed the presence of four large peaks, the largest of which was the required product. Further purification was carried out using a Pye-Unicam 105 preparative gas chromatograph. A 12', 25% squalane column was used initially at 80°C and 20 psi nitrogen carrier gas pressure.

The temperature was reduced to 35°C for a second purification and a 12', 25% tritolylphosphate column was finally used at room temperature and a nitrogen carrier gas pressure of 8 psi.

The 1,1,1-trifluoropentane was introduced onto the vacuum line and further purification by trap to trap distillation was carried out before being stored in a glass finger.

APPARATUS

The reactions were carried out on a conventional vacuum line made of "pyrex" with greaseless fittings as shown in figure 1 except for a few modifications. For these experiments an Edwards capsule guage (0 → 100 torr) was added to the small manifold alongside the glass storage bulbs. The glass spiral guage was also used to measure reactants when more than 100 torr was required. The glass bulbs, I and II were used to measure reactants along with the reaction vessel III which was identical to that used in photolytic experiments described in section 1.

The furnace used was the same as in previous experiments, the power again being supplied by a Variac transformer (0 → 250 volts) and the temperature in the furnace was measured with a mercury in glass thermometer.

The light source was a Hanovia UVS 220 medium pressure mercury arc lamp, situated so as to be able to impinge directly onto the reaction vessel.

Although the "pyrex" reaction vessel was capable of acting as a filter for light wavelength less than 2,800 Å, additional filters were placed into the circular hole in the furnace. These consisted of two "Pyrex" circular plates approximately 1/16" thick.

The vacuum was monitored at all times by the use of a high frequency tesla coil.

PROCEDURE

Before each experiment was carried out the vacuum line was pumped out for at least one hour with the trap immersed in liquid nitrogen. The reactants were all thoroughly degassed before each run.

Photolysis of trifluoromethyl iodide and *n*-butane (1st series)

When a good vacuum existed in the line, the manifold was isolated from the pumps and trifluoromethyl iodide was allowed to expand into the reaction vessel, manifold and capsule guage until the required pressure had registered on the guage. The reaction vessel was then isolated and the trifluoromethyl iodide outwith it was condensed back into its storage bulb by placing a "Dewar" of liquid nitrogen around the cold finger connected to the storage bulb. The storage

bulb was then isolated and the line was again pumped down to a high vacuum.

The same procedure was then repeated for *n*-butane. This time however the reaction vessel remained isolated and the *n*-butane was allowed to expand into one of the measuring bulbs.

The reaction vessel was immersed in liquid nitrogen and thoroughly degassed. The *n*-butane in the measuring bulb was then allowed to condense into the reaction vessel, at least 20 minutes being allowed for this to be completed, a tesla coil being employed to ensure that complete condensation had occurred. The contents of the reaction vessel were again thorougly degassed before being isolated from the main manifold. The contents of the reaction vessel were then warmed up to room temperature and again immersed in liquid nitrogen and thoroughly degassed. The furnace which had been previously heated to the required reaction temperature was then placed around the reaction vessel. A shutter was placed between the reaction vessel and the light source and the mercury lamp was switched on. Thirty minutes were allowed for the temperature in the oven to equilibriate and the shutter was removed and the temperature noted.

When photolysis had occurred for the required length of time the lamp was switched off. The reaction products were condensed into a glass finger attached to the main manifold which had previously been pumped down. At least 30 minutes were allowed for all the material to condense into the glass finger. The finger was then isolated and removed for analysis.

Photolysis of *n*-butyl fluoride, *n*-butane (2nd series) and 1,1,1-trifluoropentane

The procedure was the same as that previously described except for a few minor modifications. In this series of experiments a pool of mercury was introduced into the reaction vessel. Care therefore had to be taken to ensure that no mercury got into any other part of the apparatus. To prevent this happening the reaction vessel was always isolated from the rest of the system when it was hot. Care also had to be taken in degassing operations and also when condensing the reaction mixture into the glass finger for analysis. This was due to the fact that material was often trapped in the pool of mercury. This was removed by swirling the pool around taking great care not to break the capillary tube connecting the reaction vessel to the main manifold.

ANALYSIS

The analysis of all the runs was carried out on a gas chromatograph with a gas density balance detector identical to that described in section 1. After using various column packings it was found that the best results were obtained with a 12' Pye Unicam preparative column using a 20% (w/w) silicone oil on 60/80 mesh Embacel packing. The reaction products were analysed in the liquid phase using a Hamilton 50µl syringe (N705) which had been

cooled in liquid nitrogen. A standard Pye Unicam 104 series injection port was incorporated into the chromatograph and oxygen free nitrogen was used as the carrier gas.

The areas of the product peaks were measured using either a Dupont 310 curve resolver or a fixed arm planimeter.

IDENTIFICATION OF PRODUCTS

Photolysis of trifluoromethyl iodide and *n*-butane (1st series)

The two expected products from these runs were 2-iodobutane and 1-iodobutane. Authentic samples of these two compounds were readily available and these were added in turn to the reactant products. This caused an enhancement of the relevant peak upon analysis by gas chromatography. To confirm the identification of the two products, a mass spectrometry/GLC analysis was carried out and the mass spectra compared with the mass spectra of authentic samples (Table 2/1).

The mass spectra were obtained on an AEI MS 902 mass spectrometer. The inlet was from a conventional Pye Unicam 104 series gas chromatograh and the same silicone oil column as used in the gas chromatographic analysis was used.

1-iodobutane				2-iodobutane			
m/e	% Reaction Product	% Authentic Sample	assignment	m/e	% Reaction Product	% Authentic Sample	assignment
27	25	23	$C_2H_3^+$	27	21	21	$C_2H_3^+$
29	52	53	$C_2H_5^+$	29	70	73	$C_2H_5^+$
39	13	9	$C_3H_3^+$	39	16	17	$C_3H_3^+$
41	35	36	$C_3H_5^+$	41	32	30	$C_3H_5^+$
57	100	100	$C_4H_9^+$	57	100	100	$C_4H_9^+$
127	12	9	I^+	127	5	5	I^+
141	4	4	CH_2I^+	140	1	2	CHI^+
155	2	3	$C_2H_4I^+$	155	4	4	$C_2H_4I^+$
184	5	5	$C_4H_9I^+$	184	4	5	$C_4H_9I^+$

TABLE 2/1

MASS SPECTRA OF PRODUCTS FROM THE REACTION OF TRIFLUOROMETHYL IODIDE WITH *n*-BUTANE

Photolysis of trifluoromethyl iodide and *n*-butyl chloride

The four expected products from these experiments were 1-chloro,1-iodobutane, 2-chloro,1-iodobutane, 3-chloro, 1-iodobutane and 4-chloro,1-iodobutane. From previous experiments [77] the expected order of elution with the analytical conditions used would be as written. Six peaks actually occurred after the reactants. Analysis by GLC/Mass Spectrometry suggested that the first two peaks were 2-iodobutane and 1-iodobutane. The other four peaks were not large enough for analysis by this method. The two iodobutanes were confirmed by the use of authentic samples as previously described.

An attempt was made to identify the 1-chloro,4-iodobutane. An authentic sample was prepared from the readily available 1,4-dichlorobutane as described.

Sodium iodide (15g) was dissolved in acetone (400ml) in a 500ml round bottomed flask connected to a reflux condenser. 1,4-dichlorobutane (15ml) was added and the reactants were refluxed for one hour. A white precipitate was formed which was filtered off using a filter funnel and cotton wool. The acetone was removed by distillation, everything above 60^{o}C being retained.

On GLC analysis under identical conditions to those used, three peaks were observed. The first had the same retention time as the starting material (1,4-dichlorobutane). The second (and largest) corresponded to the sixth peak in the previous analytical runs and the third peak which was very small was probably due to

1,4-diiodobutane. The second peak was identified by Mass Spectrometry as being 1-chloro,4-iodobutane. It seems likely therefore that the four chloro,iodobutanes were eluted in the expected order.

Photolysis of trifluoromethyl iodide and *n*-butyl fluoride

Authentic samples were not available for the products of this reaction. Identification was therefore carried out using GLC/Mass Spectrometry. The expected order of elution of the products based on the previous work was 1-fluoro,1-iodobutane, 1-fluoro,2-iodobutane, 1-fluoro,3-iodobutane and 1-fluoro,4-iodobutane. This order was in fact found to be correct. The results from the GLC/Mass Spectrometry analysis are given in Table 2/2.

Photolysis of trifluoromethyl iodide and 1,1,1-trifluoropentane

Again authentic samples were not available and identification was carried out using GLC/Mass Spectrometry only. The expected order of elution of the products was 1,1,1-trifluoro,2-iodopentane, 1,1,1-trifluoro,3-iodopentane, 1,1,1-trifluoro,4-iodopentane and 1,1,1-trifluoro,5-iodopentane. Four peaks occurred, the first of which was very small. It was not possible to obtain a mass spectrum of this compound, suspected to be 1,1,1-trifluoro,2-iodopentane. The next three peaks were in fact the ones expected. The mass spectra of these are given in Table 2/3.

TABLE 2/2 : MASS SPECTRA OF THE PRODUCTS FROM THE REACTION OF TRIFLUOROMETHYL IODIDE AND *n*-BUTYL FLUORIDE

1-fluoro,1-iodobutane			1-fluoro,2-iodobutane			1-fluoro,3-iodobutane			1-fluoro,4-iodobutane		
m/e	%	assignment	m/e	%	assignment	m/e	%	assignment	m/e	%	assignment
26	8	$C_2H_2^+$	26	8	$C_2H_2^+$	26	3	$C_2H_2^+$	26	8	$C_2H_2^+$
27	43	$C_2H_3^+$	27	38	$C_2H_3^+$	27	23	$C_2H_3^+$	27	45	$C_2H_3^+$
29	100	$C_2H_5^+$	29	86	$C_2H_5^+$	29	61	$C_2H_5^+$	29	8	$C_2H_5^+$
31	2	CF^+	33	6	CH_2F^+	33	5	CH_2F^+	33	7	CH_2F^+
33	6	CH_2F^+	39	17	$C_3H_3^+$	38	2	$C_3H_2^+$	39	20	$C_3H_3^+$
38	2	$C_3H_2^+$	41	20	$C_3H_5^+$	39	12	$C_3H_3^+$	41	20	$C_3H_5^+$
40	7	$C_3H_4^+$	44	6	C_2HF^+	41	13	$C_3H_5^+$	44	11	C_2HF^+
41	10	$C_3H_5^+$	45	3	$C_2H_2F^+$	42	2	$C_3H_6^+$	46	7	$C_2H_3F^+$
44	8	C_2HF^+	46	9	$C_2H_3F^+$	44	1	C_2HF^+	47	50	$C_2H_4F^+$
45	3	$C_2H_2F^+$	47	51	$C_2H_4F^+$	45	2	$C_2H_2F^+$	53	6	$C_4H_5^+$

TABLE 2/2 continued

| | | |

TABLE 2/2 continued

153	1	$C_2H_2I^+$
155	1	$C_2H_4I^+$
202	21	$C_4H_8FI^+$

173	1	$C_2H_3FI^+$
202	5	$C_4H_8FI^+$

TABLE 2/3 : MASS SPECTRA OF THE PRODUCTS FROM THE REACTION OF TRIFLUOROMETHYL IODIDE AND 1,1,1-TRIFLUOROPENTANE

1,1,1-trifluoro,3-iodopentane			1,1,1-trifluoro,4-iodopentane			1,1,1-trifluoro,5-iodopentane		
m/e	%	assignment	m/e	%	assignment	m/e	%	assignment
27	45	$C_2H_3^+$	26	7	$C_2H_2^+$	26	11	$C_2H_2^+$
29	60	$C_2H_5^+$	27	31	$C_2H_3^+$	27	64	$C_2H_3^+$
41	95	$C_3H_5^+$	29	41	$C_2H_5^+$	29	32	$C_2H_5^+$
47	15	$C_2H_4F^+$	39	23	$C_3H_3^+$	39	32	$C_3H_3^+$
51	10	$C_4H_3^+$	41	69	$C_3H_5^+$	41	100	$C_3H_5^+$
59	35	$C_3H_4F^+$	42	7	$C_3H_6^+$	47	21	$C_2H_4F^+$
61	60	$C_3H_6F^+$	47	13	$C_2H_4F^+$	51	16	$C_4H_3^+$
77	50	$C_3H_3F_2^+$	51	9	$C_4H_3^+$	55	27	$C_4H_7^+$
85	25	$C_5H_6F^+$	55	22	$C_4H_7^+$	59	32	$C_3H_4F^+$
105	45	$C_5H_7F_2^+$, $C_4F_3^+$	59	22	$C_3H_4F^+$	61	74	$C_3H_6F^+$
124	10	$C_5H_7F_3^+$	61	48	$C_3H_6F^+$	77	64	$C_3H_3F_2^+$

TABLE 2/3 continued

| | | |

DETAILS OF REACTIONS

Trifluoromethyl iodide and *n*-butane (1st series)

Analysis by gas chromatography

nitrogen carrier gas, flow rate 50mls/min,

oven temperature 100°C

Irradiation time 180min

Reactant pressures Trifluoromethyl iodide 100mm

n-Butane 10mm

Temp (°C)	2[*n*-BuI]/3[*sec*-BuI]
76 (3)	0.128
91 (4)	0.125
107 (8)	0.144
120 (7)	0.151
126 (2)	0.154
155 (1)	0.170
166 (6)	0.161
190 (5)	0.201

A least squares plot of log 2[*n*-BuI]/3[*sec*-BuI] against $10^3/T$ gave a gradient of -0.260 (± 0.091) and an intercept of -0.1639 (± 0.0362)

TABLE 2/4 : VARIATION OF TEMPERATURE

Trifluoromethyl iodide and *n*-butyl fluoride

Analysis by gas chromatography

nitrogen carrier gas flow rate 100mls/min,

oven temperature 120°C

Irradiation time 10min

Reactant pressure trifluoromethyl iodide 50mm

n-butyl fluoride 50mm

Temp (°C)	[1-F,1-I But] / [1-F,3-I But]	[1-F,2-I But] / [1-F,3-I But]	2[1-F,4-I But] / 3[1-F,3-I But]	
30	0.147	0.210	-	(6)
49.5	0.161	0.199	0.080	(7)
56	0.171	0.220	0.079	(5)
67	0.158	0.212	0.123	(3)
76	0.175	0.220	0.081	(4)
88	0.178	0.198	0.087	(2)
99	0.182	0.204	0.090	(1)
119	-	-	0.097	(8)
144	-	-	0.113	(9)

A least squares plot of log[1-F,1-I But]/[1-F,3-I But] against $10^3/T$ gave a gradient of -0.1419 (± 0.0920) and an intercept of -0.3580 (± 0.0310) A least squares plot of log[1-F,2-I But]/[1-F,3-I But] against $10^3/T$ gave a gradient of +0.0171 (± 0.1148) and an intercept of -0.7309 (± 0.0387) A least squares plot of log 2[1-F,4-I But]/3[1-F,3-I But] against $10^3/T$ gave a gradient of -0.2093 (± 0.0799) and an intercept of -0.4715 (± 0.0285).

TABLE 2/5 : VARIATION OF TEMPERATURE

Trifluoromethyl iodide and *n*-butane (2nd series)

Analysis by gas chromatography

nitrogen carrier gas flow rate 75mls/min

oven temperature 100°C.

Irradiation time 10min → 15 min

Reactant pressure trifluoromethyl iodide 60mm

n-butane 60mm.

Temp (°C)	2[*n*-BuI]/3[*sec*-BuI]
28 (7)	0.0555
50 (6)	0.0584
53 (2)	0.0591
62.5 (3)	0.0628
64 (9)	0.0602
64.5 (8)	0.0639
77.5 (4)	0.0667
87 (5)	0.0708
100.5 (1)	0.0778

A least squares plot of log 2[*n*-BuI]/3[*sec*-BuI] against $10^3/T$ gave a gradient of -0.230 (± 0.080) and an intercept of -0.5111 (± 0.027)

TABLE 2/6 : VARIATION OF TEMPERATURE

Trifluoromethyl iodide and 1,1,1-trifluoropentane

Analysis by gas chromatography

nitrogen carrier gas flow rate 75mls/min

oven temperature 110°C

Irradiation time 10min

Reactant pressure trifluoromethyl iodide 60mm

1,1,1-trifluoropentane 60mm

Temp (°C)	[1,1,1-TF,2-I Pent] / [1,1,1-TF,4-I Pent]	[1,1,1-TF,3-I Pent] / [1,1,1-TF,4-I Pent]	2[1,1,1-TF,5-I Pent] / 3[1,1,1-TF,4-I Pent]	
75	-	0.1974	0.0842	(7)
88	-	0.2126	0.0906	(3)
112.5	0.0096	0.2478	0.0986	(2)
122	0.0106	0.2590	0.0992	(1)
148.5	0.0069	0.2738	0.1139	(4)
171	0.0085	0.3037	0.1256	(5)
198.5	0.0074	0.3320	0.1394	(6)

A least squares plot of log [1,1,1-TF,2-I Pent]/[1,1,1-TF,4-I Pent] against $10^3/T$ gave a gradient of 0.2771 (± 0.3864) and an intercept of -2.7291 (± 0.1623)

A least squares plot of log [1,1,1-TF,3-I Pent]/[1,1,1-TF,4-I Pent] against $10^3/T$ gave a gradient of -0.2931 (± 0.0354) and an intercept of +0.1433 (± 0.0141)

A least squares plot of log 2[1,1,1-TF,5-I Pent]/3[1,1,1-TF,4-I Pent] against $10^3/T$ gave a gradient of -0.2862 (± 0.0442) and an intercept of -0.2592 (± 0.0176).

TABLE 2/7 : VARIATION OF TEMPERATURE

RESULTS

n-Butane (1st series)

In the study of trifluoromethyl radicals the use of trifluoromethyl iodide as the source of radicals has the advantage that the butyl radicals formed are scavenged as *n*-butyl and *sec*-butyl iodides. Analysis of these iodides allows us to calculate the Arrhenius parameters for trifluoromethyl attack at the specific sites in *n*-butane.

The reactions can be represented as follows

$$CF_3I \longrightarrow CF_3\cdot + I \qquad (1)$$

$$2CF_3\cdot \longrightarrow C_2F_6 \qquad (2)$$

$$CF_3\cdot + n\text{-}C_4H_{10} \longrightarrow CF_3H + n\text{-}C_4H_9\cdot \qquad (3)$$

$$\longrightarrow CF_3H + sec\text{-}C_4H_9\cdot \qquad (4)$$

$$n\text{-}C_4H_9\cdot + CF_3I \longrightarrow n\text{-}C_4H_9I + CF_3\cdot \qquad (5)$$

$$sec\text{-}C_4H_9\cdot + CF_3I \longrightarrow sec\text{-}C_4H_9I + CF_3\cdot \qquad (6)$$

According to the above reaction scheme the amount of trifluoromethane produced should equal the amount of butyl iodide produced. Approximate measurements of the trifluoromethane formation in certain runs was consistent with this. No evidence existed for the presence of combination or disproportionation reactions by the butyl radicals formed.

The chromatogram shows that there was no evidence of any other reaction product being present besides those accounted for by the reactions (1) to (6).

The treatment of the results involves the application of the steady-state hypothesis to the reaction scheme (1) to (6).

$$\frac{d[n\text{-}C_4H_9\cdot]}{dt} = k_3[CF_3\cdot][n\text{-}C_4H_{10}] - k_5[CF_3I][n\text{-}C_3H_9\cdot] = 0 \qquad (7)$$

$$\frac{d[sec\text{-}C_4H_9\cdot]}{dt} = k_4[CF_3\cdot][n\text{-}C_4H_{10}] - k_6[CF_3I][sec\text{-}C_4H_9\cdot] = 0 \qquad (8)$$

The rates of formation of the butyl iodides are given by

$$\frac{d[n\text{-}C_4H_9I]}{dt} = k_5[n\text{-}C_4H_9\cdot][CF_3I] = k_3[CF_3\cdot][n\text{-}C_4H_{10}] \qquad \text{(from (7))}$$

$$\frac{d[sec\text{-}C_4H_9I]}{dt} = k_6[sec\text{-}C_4H_9\cdot][CF_3I] = k_4[CF_3\cdot][n\text{-}C_4H_{10}] \qquad \text{(from (8))}$$

Hence

$$\frac{d[n\text{-}C_4H_9I]}{d[sec\text{-}C_4H_9I]} = \frac{k_3[CF_3\cdot][n\text{-}C_4H_{10}]}{k_4[CF_3\cdot][n\text{-}C_4H_{10}]}$$

If the extent of reaction is small the right hand side of this equation remains approximately constant, and on integration.

$$\frac{[n\text{-}C_4H_9I]_f}{[sec\text{-}C_4H_9I]_f} = \frac{k_3[n\text{-}C_4H_{10}]_i}{k_4[n\text{-}C_4H_{10}]_i}$$

Therefore

$$\frac{k_3}{k_4} = \frac{[n\text{-}C_4H_9I]_f}{[sec\text{-}C_4H_9I]_f}$$

To express the rate constant ratio per hydrogen atom we can use the term Relative Selectivity as previously defined

$$RS^n_{sec} = \frac{k_n}{k_{sec}} = \frac{2[n\text{-}C_4H_9I]}{3[sec\text{-}C_4H_9I]} \qquad (9)$$

Using the Arrhenius equation

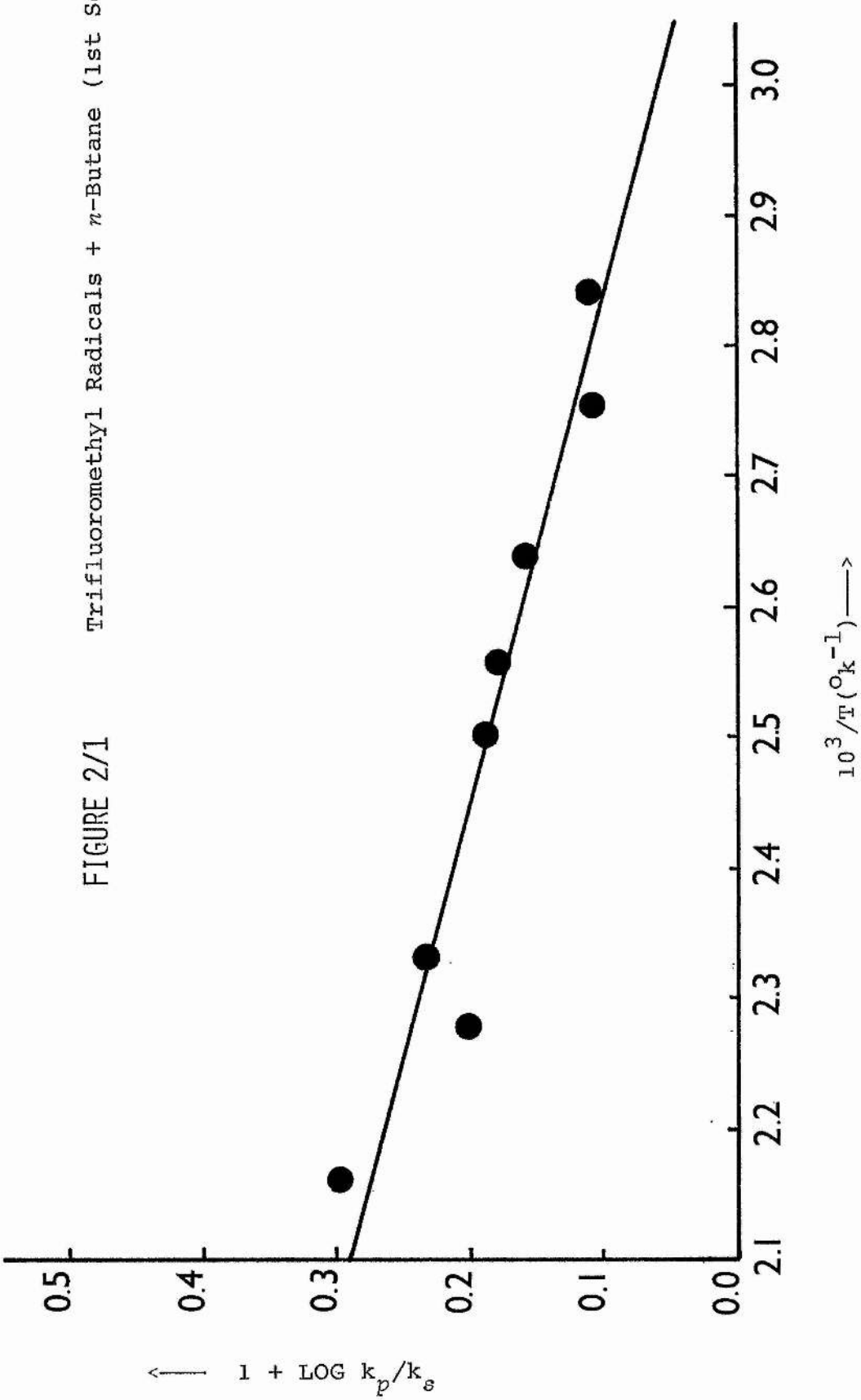
$$k = Ae^{-E/RT}$$

equation (9) can be expressed in the form

$$\log RS^n_{sec} = \log k_n/k_s = \log A_n/A_s + \frac{E_s - E_n}{2.303\ RT} \qquad (10)$$

The results obtained from these experiments are given in table 2/4. Using these results the quantity $\log RS^n_{sec}$ was plotted against $10^3/T$ and gave a straight line (figure 2/1). From the slope of this line a value of $E_s - E_n = -1.19$ kcals was obtained and from the intercept on the y-axis we obtained $\log A_n/A_s = -0.1639$.

FIGURE 2/1 Trifluoromethyl Radicals + *n*-Butane (1st Series)



n-Butylchloride (1st series)

The two largest products were *n*-butyl iodide and *sec*-butyl iodide. The four chloro,iodobutanes were also present but in much smaller quantities. The reaction time for these experiments was about five hours and even after this length of time the products were only just measurable. No reason could be seen for the presence of the two butyl iodides and obviously no kinetic data could be obtained without their presence being accounted for.

n-Butyl Fluoride

The initial runs carried out with trifluoromethyl iodide and *n*-butyl fluoride proved unsuccessful for the extraction of kinetic data. Very long runs of up to twelve hours were carried out and the percentage of reactions was still far too small to enable the product peaks to be measured accurately. The amount of reactants was altered from 100mm trifluoromethyl iodide and 10mm *n*-butyl fluoride to 55mm of each reactant in an attempt to increase the yield. This proved successful in so much as to increase the amount of reaction, unfortunately many peaks occurred on the chromatograph in the region where the fluoro,iodobutanes were expected to be recorded. An attempt was made to separate these products using gas chromatography. Several different columns were used, silicone oil (12',20%),

tritolylphosphate (12',25%), squalane (12',25%), dinonylphosphate (12',20%), and Chromosorb 102. Complete separation could not be achieved although the best separation was obtained with the silicone oil column.

Eight peaks occurred in the region where the four expected products would be seen, two other large peaks being eluted somewhat earlier. A mass spectrometry/GLC analysis revealed that these two large peaks were *sec*-butyl iodide and *n*-butyl iodide. The analysis also revealed the presence of a large amount of but-I-ene.

An experiment was carried out to see if and how hydrogen iodide reacted with *n*-butyl fluoride. A run was carried out in the dark at 80°C for sixteen hours using 1mm hydrogen iodide and 110mm *n*-butyl fluoride. Analysis of the reaction products showed that large amounts of but-I-ene, *sec*-butyl iodide and *n*-butyl iodide had been produced. There seems little doubt that hydrogen iodide produced in the photolytic runs is responsible for the production of but-I-ene which in turn is responsible for the production of the two butyl iodides and addition products found amongst the reaction products.

The hydrogen iodide was probably produced by hydrogen abstraction reactions involving excited iodine atoms. At 2537 Å, which is the main line in the mercury spectrum responsible for the photolysis of trifluoromethyl iodide, an excited iodine atom ($^2P_{1/2}$) is produced [79]. The excited energy ($^2P_{3/2} \longrightarrow {}^2P_{1/2}$) is 22 kcal mol^{-1} and this extra energy enables hydrogen abstraction by iodine to occur.

If the excited iodine atoms were removed before they abstracted hydrogen from the *n*-butyl fluoride it should be possible to obtain a 'clean' reaction. Mercury was therefore introduced into the reaction

vessel to 'mop up' the excited iodine atoms.

The first run carried out in the presence of mercury was analysed and a very large amount of trifluoromethane was found. Far too much reaction had taken place and instead of the four fluoro, iodobutanes being seen on the chromatogram, at least 25 products were found. The reaction time was reduced from twelve hours to ten minutes and four easily measurable well separated fluoro,iodobutanes were seen.

The reactions occurring can be represented as follows:

$$CF_3I \xrightarrow{h\nu} CF_3\cdot + I \qquad (11)$$

$$2I + M \longrightarrow I_2 + M$$

$$2I + Hg \longrightarrow HgI_2 \qquad (12)$$

$$2CF_3\cdot \longrightarrow C_2F_6 \qquad (13)$$

$$CF_3\cdot + n\text{-}C_4H_9F \longrightarrow CH_3CH_2CH_2\dot{C}HF + CF_3H \qquad (14)$$

$$\longrightarrow CH_3CH_2\dot{C}HCH_2F + CF_3H \qquad (15)$$

$$\longrightarrow CH_3\dot{C}HCH_2CH_2F + CF_3H \qquad (16)$$

$$\longrightarrow \dot{C}H_2CH_2CH_2CH_2F + CF_3H \qquad (17)$$

$$CH_3CH_2CH_2\dot{C}HF + CF_3I \longrightarrow CH_3CH_2CH_2CHFI + CF_3\cdot \quad (18)$$

$$CH_3CH_2\dot{C}HCH_2F + CF_3I \longrightarrow CH_3CH_2CHICH_2F + CF_3\cdot \quad (19)$$

$$CH_3\dot{C}HCH_2CH_2F + CF_3I \longrightarrow CH_3CHICH_2CH_2F + CF_3\cdot \quad (20)$$

$$\dot{C}H_2CH_2CH_2CH_2F + CF_3I \longrightarrow CH_2ICH_2CH_2CH_2F + CF_3\cdot \quad (21)$$

The amount of trifluoromethane formed was approximately equal to the total amount of fluoro,iodobutane formation. The chromatogram showed no evidence of the presence of other major products.

The selectivity of the trifluoromethyl radicals to hydrogen abstraction has been found relative to the hydrogen atoms γ to the fluorine substituent. Equation (10) therefore can be written in the forms

$$\log R.S._{\dot{\gamma}}^{\alpha} = \log k_{14}/k_{16} = \log A_{14}/A_{16} + \frac{E_{16} - E_{14}}{2.303\,RT} \quad (22)$$

$$\log R.S._{\dot{\gamma}}^{\beta} = \log k_{15}/k_{16} = \log A_{15}/A_{16} + \frac{E_{16} - E_{15}}{2.303\,RT} \quad (23)$$

$$\log R.S._{\dot{\gamma}}^{\delta} = \log k_{17}/k_{16} = \log A_{17}/A_{16} + \frac{E_{16} - E_{17}}{2.303\,RT} \quad (24)$$

where the α, β, γ and δ hydrogens are

$$\overset{\delta}{CH_3} \text{ —— } \overset{\gamma}{CH_2} \text{ —— } \overset{\beta}{CH_2} \text{ —— } \overset{\alpha}{CH_2F}$$

The results obtained from these experiments are given in table 2/5. Using these results, log R.S.$^{\alpha}_{\gamma}$, log R.S.$^{\beta}_{\gamma}$ and log R.S.$^{\delta}_{\gamma}$ were plotted against $10^3/T$ and three straight lines were obtained (figure 2/2). From the slopes and intercepts on the y-axis the following values were obtained. $E_{16} - E_{14} = -0.649$ kcals, $\log A_{14}/A_{16} = -0.3582$; $E_{16} - E_{15} = +0.0787$ kcals, $\log A_{15}/A_{16} = -0.7312$; $E_{16} - E_{17} = -0.9578$ kcals, $\log A_{17}/A_{16} = -0.4715$.

n-Butane (2nd series)

These experiments were carried out using the same conditions as those used in the reactions with *n*-butyl fluoride. The only difference between these runs and those carried out in the first series of experiments was the presence of mercury in the reaction vessel, the reactant pressures and the length of reaction time.

The products were the same as those obtained in the first series. The reaction time was greatly reduced during these experiments to obtain the same percentage reaction.

Using equation (10) and the results from these experiments (table 2/6) a plot of log R.S.$^{n}_{sec}$ against $10^3/T$ gave a straight line (figure 2/3). From this plot a value for $E_s - E_n$ of -1.052 kcals was obtained and also a value for $\log A_n/A_s$ of -0.5111.

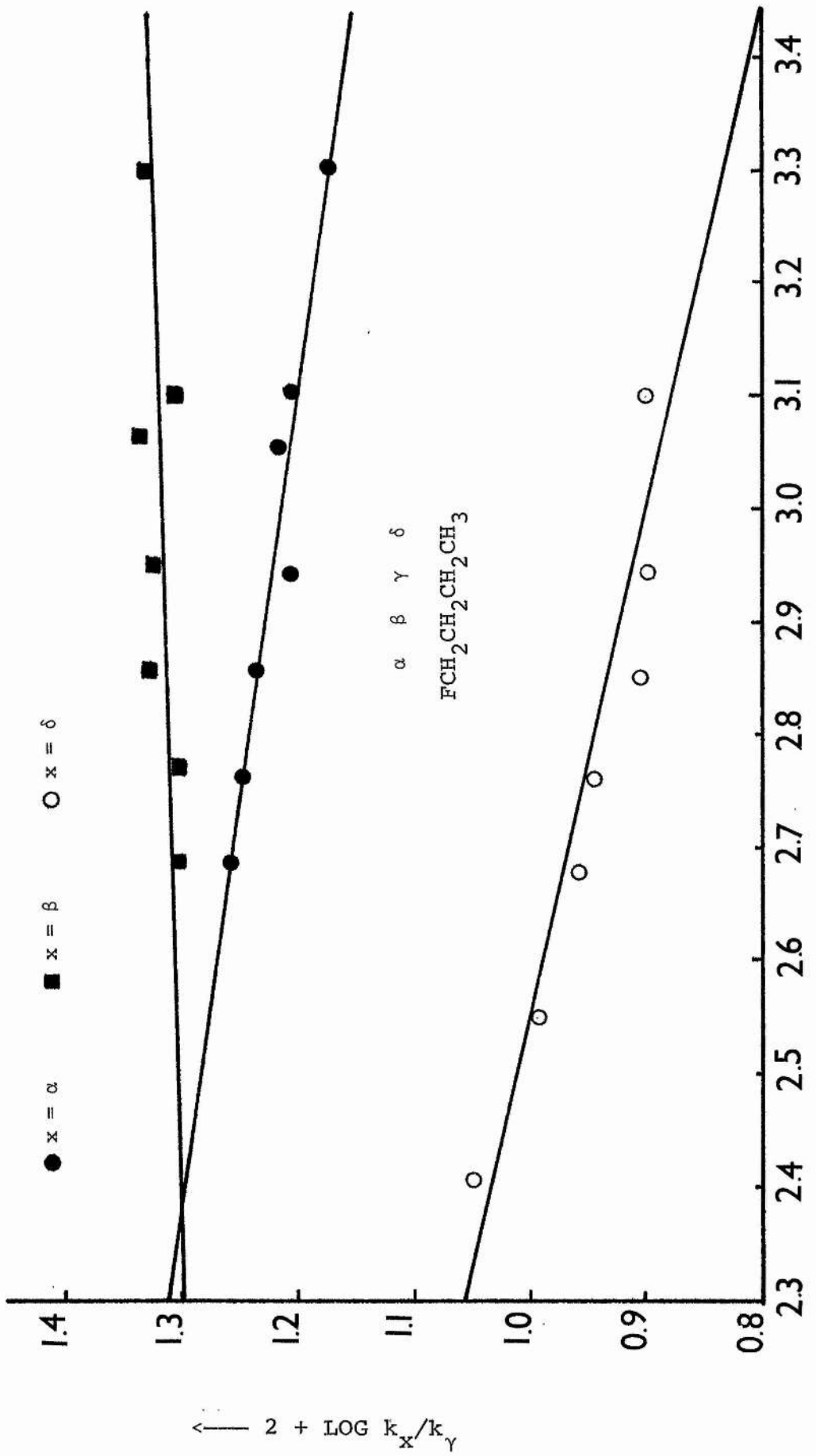


FIGURE 2/2 Trifluoromethyl Radicals + *n*-Butyl Fluoride

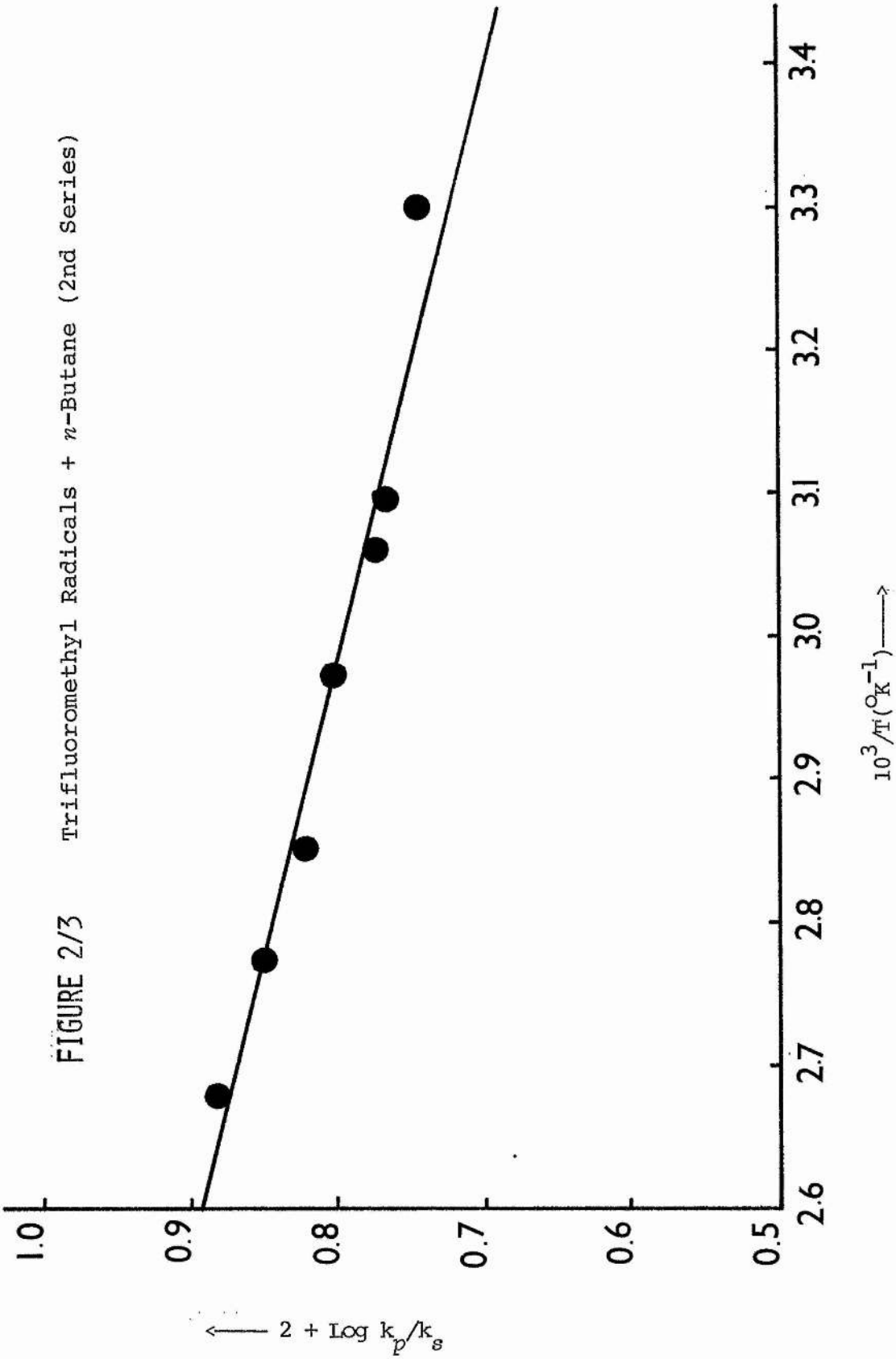


FIGURE 2/3
Trifluoromethyl Radicals + n-Butane (2nd Series)
1.0
0.9
0.8
0.7
0.6
0.5
2.6
2.7
2.8
2.9
3.0
3.1
3.2
3.3
3.4
← 2 + Log k_p/k_s
$10^3/T(^oK^{-1})$ →

n-Butyl Chloride (2nd series)

As successful results were obtained for *n*-butyl fluoride by the introduction of mercury into the reaction vessel, runs carried out with *n*-butyl chloride using this technique are also likely to be successful. The same conditions as those used in the experiments with trifluoromethyl iodide and *n*-butyl fluoride were used but unfortunately the results were very similar to those obtained for the first series of experiments. Two large peaks, *sec*-butyl iodide and *n*-butyl iodide appeared on the chromatogram and the amount of reaction to produce the chloro,iodobutanes was very small. Different reactant pressures, reaction times and lamp intensities were tried but it was not possible to reduce the amount of butyl iodide produced or increase to any great extent the production of the chloro,iodobutanes.

I,I,I-Trifluoropentane

Identical conditions to those employed in the reactions for *n*-butyl fluoride were found to be successful with 1,1,1-trifluoropentane. The reaction time was however increased so as to obtain a good product yield.

The chromatogram showed that no other major products were present. The separation of 1,1,1-trifluoro,2-iodopentane from 1,1,1-trifluoro,3-iodopentane proved to be difficult particularly

since the amount produced of the former was very small indeed.

If the four different hydrogen atoms in 1,1,1-trifluoropentane are represented thus

$$\overset{\alpha}{CF_3} \text{ —— } \overset{\beta}{CH_2} \text{ —— } \overset{\gamma}{CH_2} \text{ —— } \overset{\delta}{CH_2} \text{ —— } CH_3$$

then equations (22) to (24) can be written as

$$\log R.S._{\gamma}^{\alpha} = \log k_{\alpha}/k_{\gamma} = \log A_{\alpha}/A_{\gamma} + \frac{E_{\gamma} - E_{\alpha}}{2.303\ RT} \qquad (25)$$

$$\log R.S._{\gamma}^{\beta} = \log k_{\beta}/k_{\gamma} = \log A_{\beta}/A_{\gamma} + \frac{E_{\gamma} - E_{\beta}}{2.303\ RT} \qquad (26)$$

$$\log R.S._{\gamma}^{\delta} = \log k_{\delta}/k_{\gamma} = \log A_{\delta}/A_{\gamma} + \frac{E_{\gamma} - E_{\delta}}{2.303\ RT} \qquad (27)$$

where k_{α} is the rate constant for the hydrogen abstraction reaction for the α position, A_{α} is the A factor for the particular reaction and E_{α} its activation energy.

The results obtained from these experiments are given in table 2/7. Plots of $\log R.S._{\gamma}^{\alpha}$, $\log R.S._{\gamma}^{\beta}$ and $\log R.S._{\gamma}^{\delta}$ against $10^3/T$ gave straight lines (figure 2/4). From the slope of the lines and the intercept on the y-axis the following values were obtained : $E_{\gamma} - E_{\alpha} = 1.268$ kcals, $\log A_{\alpha}/A_{\gamma} = -2.729$; $E_{\gamma} - E_{\beta} = -1.341$ kcals, $\log A_{\beta}/A_{\gamma} = 0.143$; $E_{\gamma} - E_{\delta} = -1.310$ kcals, $\log A_{\delta}/A_{\gamma} = -0.2592$.

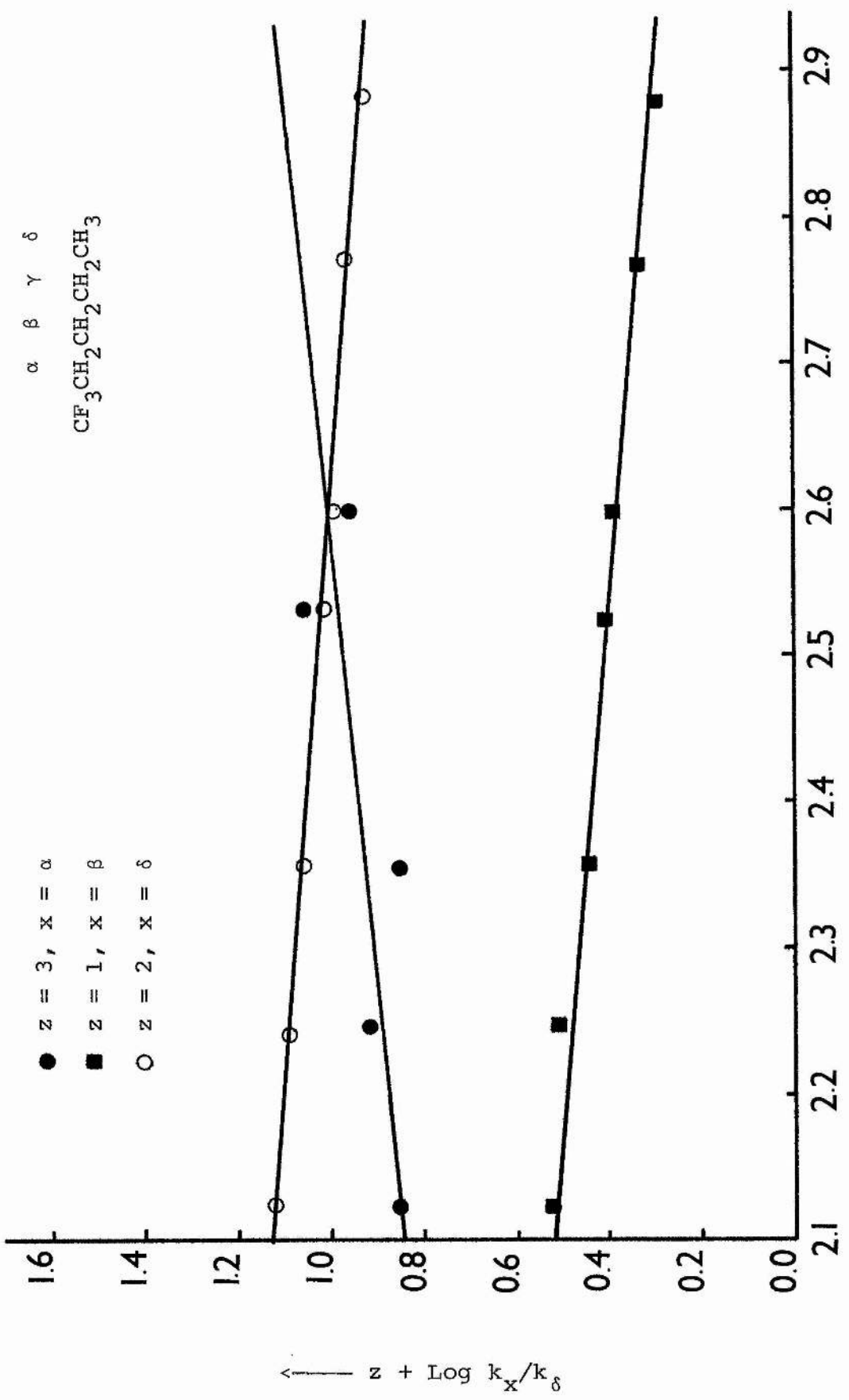


FIGURE 2/4 Trifluoromethyl Radicals + 1,1,1-Trifluoropentane

SECTION II

HYDROGEN ABSTRACTION REACTIONS OF METHYL RADICALS

INTRODUCTION

The early work carried out on the hydrogen abstraction reactions of methyl radicals was reviewed by Trotman-Dickenson [67]. Methyl radicals have received more attention than any other free radical or atom although little is known about the hydrogen abstraction reactions of methyl radicals at specific sites within a molecule.

Methyl radicals have been produced both thermally and photolytically in hydrogen abstraction studies. Thermolysis has the disadvantage that decomposition has a large activation energy. Di-*tert*-butyl peroxide has been extensively used as a thermal source of methyl radicals. The decomposition has an activation energy of 38 kcal mol^{-1} and it is only suitable as a source within the temperature range 130-170°C. Other sources include many organometallic compounds such as dimethylmercury, dimethylcadmium and tetramethyllead.

As in the analogous production of trifluoromethyl radicals, the most used photolytic source for methyl radicals is acetone. Other photolytic sources which have been used include azomethane, dimethylmercury, acetaldehyde, biacetyl and methyl iodide. Acetone has the advantages of being thermally stable up to 300°C, readily available, and the production of carbon monoxide serves as a measure of methyl radical production. Azomethane has also been extensively used although it has disadvantages over acetone in that methyl radicals tend to add to the azomethane and also it is a gas at room temperature and unstable to sunlight.

Acetone-d_6 has been extensively used as a source of methyl-d_3 radicals in the study of hydrogen abstraction reactions. When deuterium is substituted for hydrogen there is an observable primary

kinetic isotope effect in hydrogen abstraction. Secondary isotope effects are however too small to observe and are usually assumed to be zero. Abstraction by methyl radicals should therefore proceed at the same rate when methyl-d_3 radicals are used. By using acetone-d_6 a reaction naturally occurring in the reaction system can be used as a reference and indeed has been in numerous studies. When acetone-d_6 is photolysed in the presence of a substrate RH the following reactions occur

$$CD_3COCD_3 \xrightarrow{h\nu} CO + 2CD_3\cdot \qquad (1)$$

$$CD_3\cdot + CD_3COCD_3 \longrightarrow CD_4 + CD_3COCD_2\cdot \qquad (2)$$

$$CD_3\cdot + RH \longrightarrow CD_3H + R\cdot \qquad (3)$$

$$2CD_3\cdot \longrightarrow C_2D_6 \qquad (4)$$

Using reaction (2) as a reference the rate constant for hydrogen abstraction, k_3, can be determined using the expression

$$k_3/k_2 = R_{CD_3H}[CD_3COCD_3]/R_{CD_4}[RH]$$

the absolute value for k_2 being:

$$k(dm^3\ mol^{-1}\ sec^{-1}) = 10^{8.6}\ \exp[-(11,400/RT)]$$

The dimerisation of methyl (methyl-d_6) radicals has also been extensively used as a reference reaction. Shepp [68] proposed a value for the rate constant of this reaction

$$k(dm^3\ mol^{-1}\ sec^{-1}) = 10^{10.34} \exp -[(0 \pm 700)/RT]$$

When non-deuterated sources of methyl radicals are used problems arise from distinguishing the source of methane formed. This problem can be illustrated by considering the photolysis of azomethane with an alkane, RH.

$$CH_3N_2CH_3 \longrightarrow 2CH_3\cdot + N_2 \qquad (5)$$

$$CH_3\cdot + CH_3N_2CH_3 \longrightarrow CH_3N_2CH_2\cdot + CH_4 \qquad (6)$$

$$CH_3\cdot + RH \longrightarrow R\cdot + CH_4 \qquad (7)$$

$$2CH_3\cdot \longrightarrow C_2H_6 \qquad (8)$$

The rates of formation of methane and ethane are given by

$$R_{CH_4} = k_6[CH_3\cdot][CH_3N_2CH_3] + k_7[CH_3\cdot][RH]$$

$$R_{C_2H_6} = k_8[CH_3\cdot]^2$$

Hence

$$\frac{R_{CH_4}}{R_{C_2H_6}^{\frac{1}{2}}} = \frac{k_6[CH_3N_2CH_3]}{k_8^{\frac{1}{2}}} + \frac{k_7[RH]}{k_8^{\frac{1}{2}}}$$

If azomethane alone were photolysed reaction (4) would not occur and therefore $k_6[CH_3N_2CH_3]/k_8^{\frac{1}{2}}$ can be determined. The absolute value for k_8 is known and hence k_7 can be determined. This approach has also been used when acetone provides the source of methyl radicals.

Jackson, McNesby and Darwent [69] studied the hydrogen abstraction reactions of methyl-d_3 radicals from tertiary, secondary and primary sites and obtained values for the activation energies of 8.03, 10.13 and 11.73 kcal mol^{-1} respectively.

Raal and Steacie [70] studied the effects of halogen substitution on hydrogen abstraction from halogenated methanes. They observed a significant decrease in the activation energy with increasing halogenation.

$$CH_3\cdot + CH_{4-n}X_n \longrightarrow CH_4 + CH_{3-n}X_n\cdot$$

For X = chlorine they obtained values for activation energies of 9.4, 7.2 and 5.8 kcal mol^{-1} for n = 1, 2 and 3 respectively and for X = fluorine and n = 1 and 2 values for activation energies of 8.7 and 6.2 kcal mol^{-1} were determined. Raal and Steacie concluded that the decrease in activation energy was due to a decrease in C-H bond

strength with increased halogenation.

Pritchard, Bryant and Thommarson [71] redetermined the activation energies for hydrogen abstraction from fluoromethanes and values of 11.8 and 10.4 kcal mol^{-1} for methyl and methylene fluoride respectively were obtained. It was suggested that the large discrepancies between the two sets of results was due to an impurity containing labile hydrogen atoms in the experiments carried out by Raal and Steacie. The conclusion that the increased reactivity was due to a decrease in bond strength was incorrect in the case of fluoromethanes as a value for $D(CF_3-H)$ of 105 kcal mol^{-1} has been determined [72], $D(CH_3-H)$ being 101 kcal mol^{-1}.

The first work on the comparison of relative rates of attack by methyl radicals at different sites within the same molecule was carried out by Tedder and Watson [73]. Methyl radicals were produced by the photolysis of azomethane. These were allowed to react with *n*-butane in the presence of methyl iodide. Methyl iodide itself was useless as a source of methyl radicals as the radicals so produced have 32 kcal mol^{-1} excess energy and are temperature independent. The relative rates of attack at the primary and secondary positions were found using this method.

$$k_s/k_p = 1.21\ (\pm\ 0.16)\exp\ 1.65(\pm\ 0.10)\text{kcal/RT}$$

The value of 1.65 kcal mol^{-1} for E_p-E_s compares with the value of 2.3 kcal mol^{-1} obtained by comparing the reactions of methyl

radicals with ethane and *n*-butane and 2.1 kcal mol^{-1} determined by Rice and Vanderslice [74] who made assumptions about kinetic isotope effects.

Tedder and Watson applied the same method to isobutane but in this case it proved unsuccessful due to the presence of dimerisation products. The same method was used however in the work described in this part of the thesis. Initially the same system studied by Watson is repeated (i.e. hydrogen abstraction from *n*-butane). The study is then extended to determine the polar effect of substituents in the hydrogen atom abstraction reactions of methyl radicals.

EXPERIMENTAL

MATERIALS

n-Butane, *n*-butyl fluoride and 1,1,1-trifluoropentane were prepared and stored as described in Part 1 of this section. Methyl iodide (Fisons) was distilled under vacuum to remove ethane and iodine produced by photodegredation. It was stored on the vacuum line in a glass finger covered in aluminium foil to keep out the light. Azomethane was supplied by a colleague [78] and was stored at liquid nitrogen temperature in a glass finger covered in aluminium foil.

All reactants underwent trap to trap distillation on introduction to the vacuum line and all were thoroughly degassed before use.

APPARATUS

The apparatus used was identical to that used in Part 1 of this section.

PROCEDURE

As in the previous part of this section before each experiment was carried out the vacuum line was pumped out for at least one hour with the trap immersed in liquid nitrogen and the reactants were all

thoroughly degassed before each run. The reactants were measured and mixed before irradiation in the same way as for the experiments with trifluoromethyl iodide.

When photolysis had occurred for the required length of time the lamp was switched off and the furnace removed from around the reaction vessel. A large Dewar of liquid nitrogen was placed around the reaction vessel and when all the condensible products had condensed the reaction vessel was pumped down. At least 30 minutes were allowed for the nitrogen produced in the reaction to be pumped away after which the reaction vessel was isolated from the main manifold and warmed up to room temperature. The remaining contents of the reaction vessel were then condensed into a glass finger attached to the main manifold which had previously been pumped down. At least 30 minutes were allowed for all the material to condense into the glass finger which was then isolated and removed for analysis of the contents.

ANALYSIS

The products of the experiments carried out in Part 1 and Part 2 which we require to analyse quantitatively are the same. The analytical conditions and equipment used is therefore the same as that described in Part 1.

IDENTIFICATION OF PRODUCTS

As the reaction products were the same as those obtained from the reactions of trifluoromethyl iodide, identification was straightforward. The analysis of the different experiments was carried out under identical conditions to those used in the first part. Therefore the order of elution of the products from the gas chromatograph will be the same and runs carried out intermittently with trifluoromethyl iodide acted as a standard check against changes in retention times.

DETAILS OF REACTIONS

Methyl radicals and *n*-butane

Analysis by gas chromatography

nitrogen carrier gas flow rate 75mls/min

oven temperature 100°C

Irradiation time 120min → 300min

Reactant pressure azomethane 2mm

methyl iodide 50mm

n-butane 180mm

Temp (^{o}C)	2[*n*-BuI]/3[*sec*-BuI]
89 (5)	0.2196
102 (1)	0.2198
135 (4)	0.2215
155 (3)	0.2247
180 (2)	0.2273

A least squares plot of log 2[*n*-BuI]/3[*sec*-BuI] against 10^{3}/T gave a gradient of -0.0273 ($\pm$ 0.0142) and an intercept of -0.5845 ($\pm$ 0.0057)

TABLE 2/8 : VARIATION OF TEMPERATURE

Methyl radicals and *n*-butyl fluoride (1st series)

Analysis by gas chromatography

nitrogen carrier gas flow rate 100mls/min

oven temperature 120^{o}C

Irradiation time 180mins

Reactant pressures azomethane 2mm

methyl iodide 50mm

n-butyl fluoride 180mm

Temp (^{o}C)	$\frac{[1\text{-F},1\text{-I But}]}{[1\text{-F},3\text{-I But}]}$	$\frac{[1\text{-F},2\text{-I But}]}{[1\text{-F},3\text{-I But}]}$	$\frac{2[1\text{-F},4\text{-I But}]}{3[1\text{-F},3\text{-I But}]}$	
85	0.8574	1.200	0.3814	(7)
95	0.8955	1.155	0.3999	(6)
116	0.8472	1.140	0.3623	(5)
135	0.8585	1.165	0.3368	(4)
146	0.9323	1.066	0.3374	(1)
182	0.8575	1.082	0.3270	(2)
208	0.8080	0.982	0.2942	(3)

A least squares plot of log [1-F,1-I But]/[1-F,3-I But] against $10^3/T$ gave a gradient of 0.0369 ($\pm$ 0.0418) and an intercept of -0.1611 ($\pm$ 0.0169)

A least squares plot of log [1-F,2-I But]/[1-F,3-I But] against $10^3/T$ gave a gradient of 0.1012 ($\pm$ 0.0562) and an intercept of -0.2030 ($\pm$ 0.0228)

A least squares plot of log 2[1-F,4-I But]/3[1+F,3-I But] against $10^3/T$ gave a gradient of 0.1618 ($\pm$ 0.0568) and an intercept of -0.8572 ($\pm$ 0.0230).

TABLE 2/9 : VARIATION OF TEMPERATURE

Methyl radicals and *n*-butyl fluoride (2nd series)

Analysis by gas chromatography

nitrogen carrier gas flow rate 100mls/min

oven temperature 120°C

Irradiation time 120min → 360min

Reactant pressures azomethane 2mm

methyl iodide 180mm

n-butyl fluoride 180mm

Temp (°C)	$\frac{[1\text{-F},1\text{-I But}]}{[1\text{-F},3\text{-I But}]}$	$\frac{[1\text{-F},2\text{-I But}]}{[1\text{-F},3\text{-I But}]}$	$\frac{2[1\text{-F},4\text{-I But}]}{3[1\text{-F},3\text{-I But}]}$	
118	1.036	1.153	0.168	(2)
134	0.974	1.141	0.184	(3)
161	0.897	0.974	0.193	(5)
166	0.836	0.887	-	(4)
188	0.800	0.740	0.211	(1)

A least squares plot of $\log [1\text{-F},1\text{-I But}]/[1\text{-F},3\text{-I But}]$ against $10^3/T$ gave a gradient of 0.2948 (± 0.0707) and an intercept of -0.7378 (±0.0300)

A least squares plot of $\log [1\text{-F},2\text{-I But}]/[1\text{-F},3\text{-I But}]$ against $10^3/T$ gave a gradient of 0.4984 (± 0.2184) and an intercept of -1.1878 (± 0.0926)

A least squares plot of $\log 2[1\text{-F},2\text{-I But}]/3[1\text{-F},3\text{-I But}]$ against $10^3/T$ gave a gradient of -0.2360 (± 0.0685) and an intercept of -0.1656 (± 0.0288)

TABLE 2/10 : VARIATION OF TEMPERATURE

Methyl radicals with 1,1,1-trifluoropentane

Analysis by gas chromatography

nitrogen carrier gas flow rate 75mls/min

oven temperature 110°C

Irradiation time 180min → 240min

Reactant pressures azomethane 3mm

methyl iodide 180mm

1,1,1-trifluoropentane 180mm

Temp	$\frac{[1,1,1\text{-TF},2\text{-I Pent}]}{[1,1,1\text{-TF},4\text{-I Pent}]}$	$\frac{[1,1,1\text{-TF},3\text{-I Pent}]}{[1,1,1\text{-TF},4\text{-I Pent}]}$	$\frac{2[1,1,1\text{-TF},5\text{-I Pent}]}{3[1,1,1\text{-TF},4\text{-I Pent}]}$
153	0.2716	0.4159	0.2738 (1)
177	0.2220	0.4077	0.2584 (3)
192	0.2672	0.3678	0.2245 (2)
211	0.3286	0.4363	0.2277 (5)
240	0.2820	0.4638	0.2299 (4)

A least squares plot of log [1,1,1-TF,2-I Pent]/[1,1,1-TF,4-I Pent] against $10^3/T$ gave a gradient of -0.1785 (± 0.4384) and an intercept of -0.1813 (± 0.2037)

A least squares plot of log [1,1,1-TF,3-I Pent]/[1,1,1-TF,4-I Pent] against $10^3/T$ gave a gradient of -0.1261 (± 0.1576) and an intercept of -0.0883 (± 0.0732)

A least squares plot of log 2[1,1,1-TF,5-I Pent]/3[1,1,1-TF,4-I Pent] against $10^3/T$ gave a gradient of +0.2092 (± 0.1798) and an intercept of -1.0656 (± 0.836).

TABLE 2/11 : VARIATION OF TEMPERATURE

RESULTS

n-Butane

Methyl iodide is unsuitable as a source of methyl radicals for competitive runs. It exhibits a continuous absorption band in the ultra violet with a maximum at 2500 Å. This band has been interpreted by Goodeve and Porret [79]. At 2537Å, the main line in the mercury spectrum responsible for the photolysis of methyl iodide, the methyl radicals have excess energy. These 'hot' methyl radicals are independent of temperature and thus have little discrimination between different reaction sites.

Azomethane can be photolysed with light of wave length 3650Å to produce methyl radicals with little excess energy. Obviously azomethane alone cannot be used to study reactions at different sites as there would be no way of distinguishing between them. It is possible however to use azomethane as an initiator and to employ methyl iodide as a chain propagator. This was the system developed by Tedder and Watson [73] and is the one used in the work described in this part of the thesis.

The reaction scheme can be written

$$CH_3\text{-}N = N\text{-}CH_3 \xrightarrow{h\nu} 2CH_3\cdot + N_2 \qquad (28)$$

$$CH_3\cdot + RH \longrightarrow CH_4 + R\cdot \qquad (29)$$

$$CH_3\cdot + R'H \longrightarrow CH_4 + R'\cdot \qquad (30)$$

$$R\cdot + CH_3I \longrightarrow RI + CH_3\cdot \qquad (31)$$

$$R'\cdot + CH_3I \longrightarrow R'I + CH_3\cdot \qquad (32)$$

$$2CH_3\cdot \longrightarrow C_2H_6 \qquad (33)$$

Applying the steady-state approximation to this scheme gives

$$\frac{k_{29}}{k_{30}} = \frac{[RI]_f}{[R'I]_f} \times \frac{[R'H]_i}{[RH]_i}$$

where f and i refer to the final and initial states. As R'H and RH are the same, in this particular case *n*-butane, RI and R'I are *n*-butyl iodide and *sec*-butyl iodide and we can write the expression

$$R.S._{sec}^{n} = \frac{k_n}{k_{sec}} = \frac{2}{3} \frac{[n\text{-BuI}]_f}{[sec\text{-BuI}]_f} \qquad (34)$$

and the relevant Arrhenius equation is

$$R.S._{sec}^{n} = \log k_n/k_s = \log A_n/A_s + \frac{E_s - E_n}{2.303\ RT} \qquad (35)$$

The reactions of methyl radicals with azomethane

$$CH_3\cdot + CH_3\text{-}N = N\text{-}CH_3 \longrightarrow CH_4 + \cdot CH_2\text{-}N = N\text{-}CH_3 \qquad (36)$$

$$CH_3\cdot + CH_3N = N\text{-}CH_3 \longrightarrow (CH_3)_2N\text{-}\dot{N}\text{-}CH_3 \qquad (37)$$

are faster than the abstraction reactions (29), (30), and these reactions are inhibited by keeping a large [Butane]/[Azomethane] ratio.

The experiments were initially carried out with no mercury present in the reaction vessel. Analysis showed however that very little reactions had taken place. Alterations of reaction conditions such as pressures and temperature had no substantial effect on increasing product concentrations and mercury was reintroduced into the reaction vessel. The analysis of the first experiment carried out in the presence of mercury showed signs of overreaction, many small product peaks appearing. Conditions were however adjusted until the right amount of reaction had taken place.

The results obtained from these experiments are give in table 2/8. Using these results the value RS^{n}_{sec} was plotted against $10^{3}/T$ and gave a straight line (figure 2/5). From the slope of the line a value for $E_s - E_n$ = -0.125 kcals was obtained and from the intercept on the y-axis we obtained log A_n/A_s = -0.5845.

n-Butyl Fluoride

The same reaction conditions were initially employed as in the experiments using *n*-butane. As in the reactions of trifluoromethyl radicals, the selectivity for the different reaction sites was measured relative to the position gamma to the substituent. Expression (35) therefore becomes

$$RS^{\alpha}_{\gamma} = \log k_{\alpha}/k_{\gamma} = \log A_{\alpha}/A_{\gamma} + \frac{E_{\gamma} - E_{\alpha}}{2.303\ RT} \qquad (38)$$

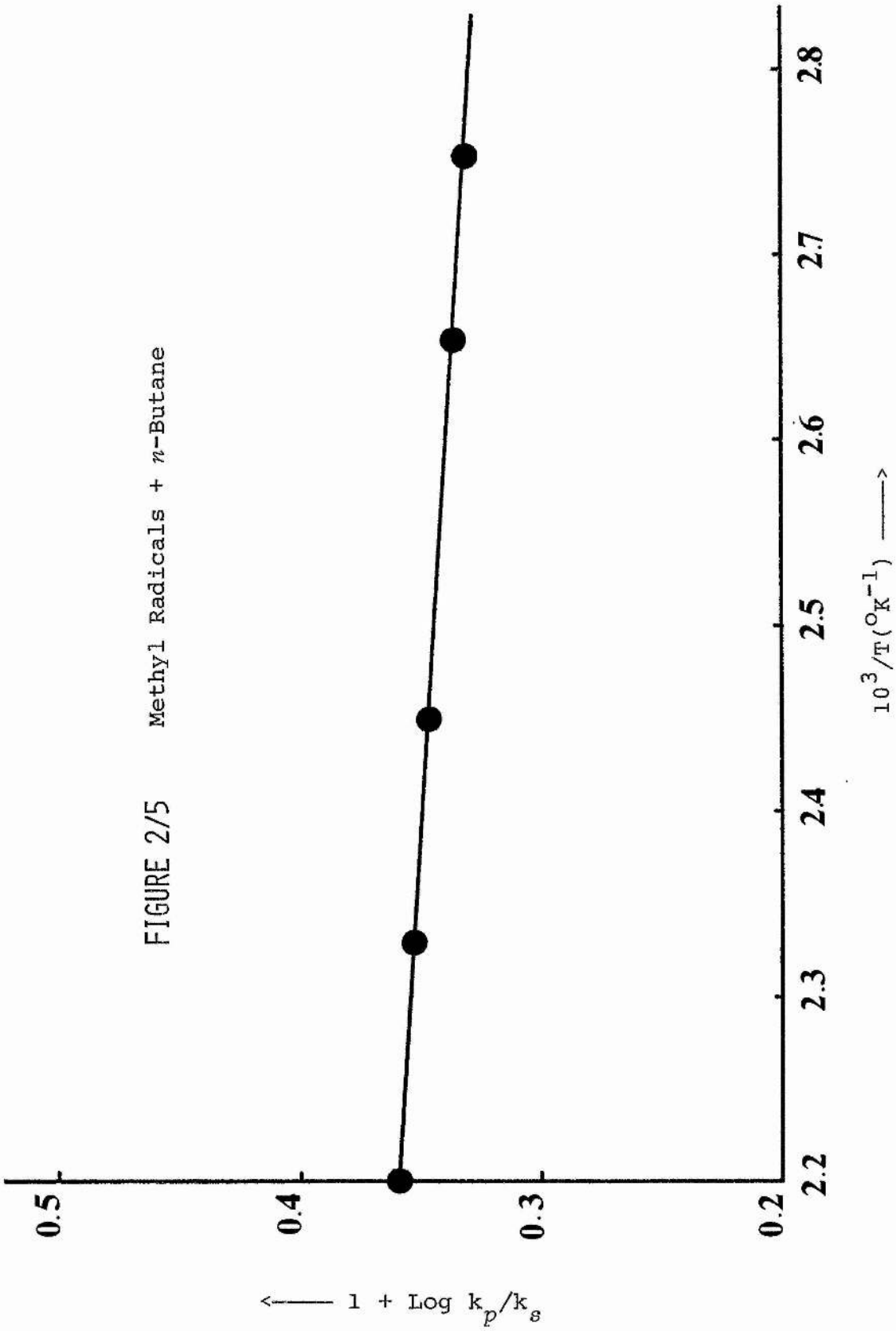


FIGURE 2/5 Methyl Radicals + *n*-Butane

$$RS^{\beta}_{\gamma} = \log k_{\beta}/k_{\gamma} = \log A_{\beta}/A_{\gamma} + \frac{E_{\gamma} - E_{\beta}}{2.303\ RT} \qquad (39)$$

$$RS^{\delta}_{\gamma} = \log k_{\delta}/k_{\gamma} = \log A_{\delta}/A_{\gamma} + \frac{E_{\gamma} - E_{\delta}}{2.303\ RT} \qquad (40)$$

where α, β, γ and δ represent the following reaction sites

$$\overset{\alpha}{F} \text{---} \overset{\beta}{CH_2} \text{---} \overset{\gamma}{CH_2} \text{---} \overset{\delta}{CH_2} \text{---} CH_3$$

As in the experiments with *n*-butane, the [*n*-butylfluoride]/[azomethane] ratio was kept high to inhibit reactions of the methyl radicals with azomethane, (36) and (37).

The results obtained in these experiments are given in table 2/9. Using these results the values RS^{α}_{γ}, RS^{β}_{γ} and RS^{δ}_{γ} were each plotted against $10^3/T$ and gave three straight lines (figure 2/6). From the slope of the lines and their interect on the y-axis the following results were obtained : $E_{\gamma} - E_{\alpha} = -0.1689$ kcals, $\log A_{\alpha}/A_{\gamma} = -0.1611$; $E_{\gamma} - E_{\beta} = -0.463$, $\log A_{\beta}/A_{\gamma} = -0.2030$; $E_{\gamma} - E_{\delta} = -0.7404$, $\log A_{\delta}/A_{\gamma} = -0.8572$.

From these results it can be seen that there is little variation with temperature on all three plots. More runs were therefore carried out with a 3-fold increase in the amount of methyl iodide present, the other quantities remaining the same.

The results obtained from these experiments are given in table 2/10. and the relevant Arrhenius plots are shown in figure 2/7. From the slope of the lines and the intercept on the y-axis the following

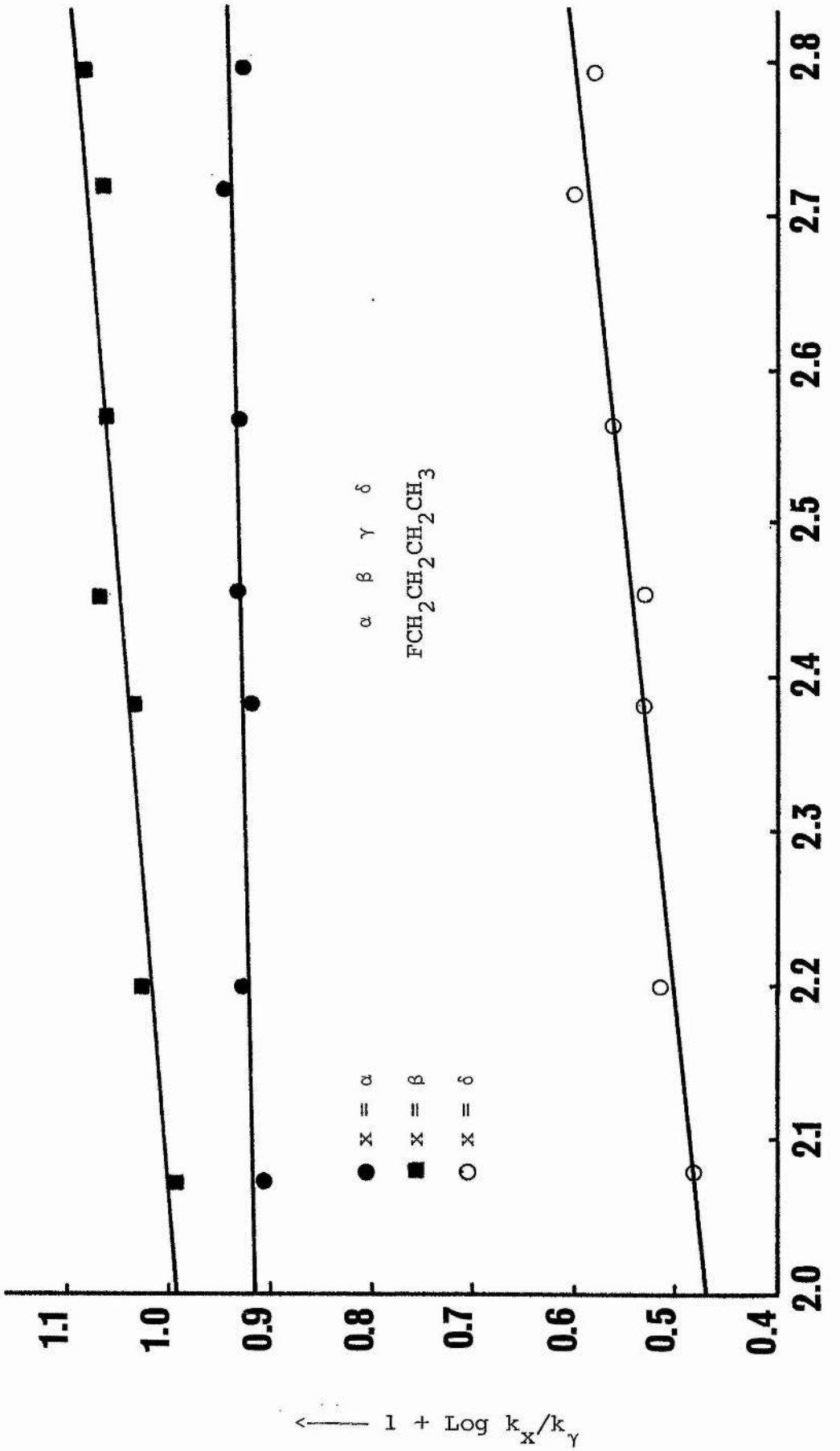


FIGURE 2/6 Methyl Radicals + *n*-Butyl Fluoride (1st Series)

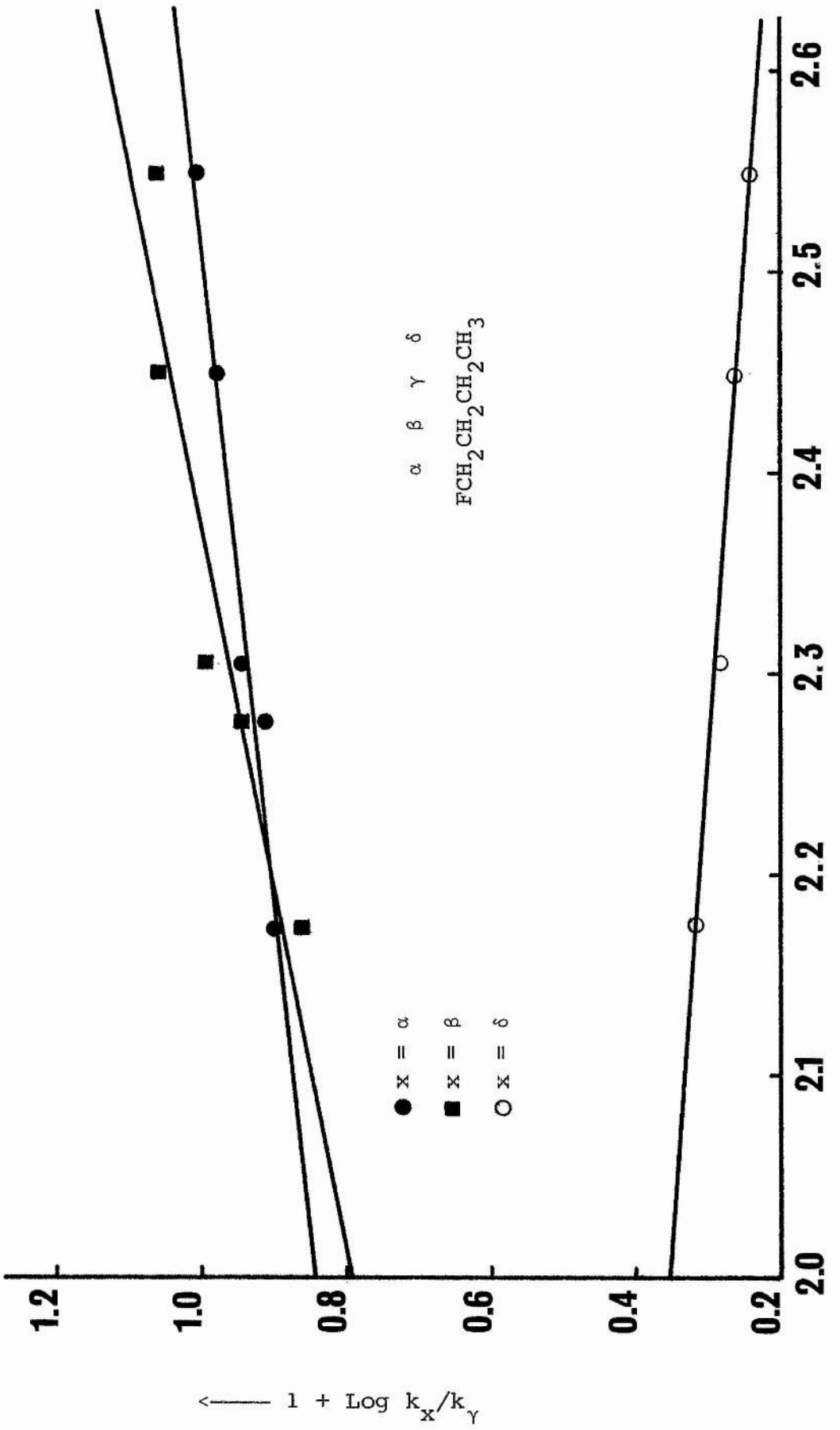


FIGURE 2/7 Methyl Radicals + *n*-Butyl Fluoride (2nd Series)

results were obtained : $E_\gamma - E_\alpha = -1.35$ kcals, $\log A_\alpha/A_\gamma = -0.738$; $E_\gamma - E_\beta = -2.28$ kcals, $\log A_\beta/A_\gamma = -1.188$; $E_\gamma - E_\delta = +1.08$ kcals, $\log A_\delta/A_\gamma = -0.1656$.

1,1,1-Trifluoropentane

The experimental conditions were the same as those used in the second series of experiments with *n*-butyl fluoride. The expressions for relative selectivity (38) to (40) are again used to calculate the Arrhenius parameters, the α, β, γ and δ positions of attack in the case of 1,1,1-trifluoropentane being:

$$\overset{\alpha}{CF_3} - CH_2 - \overset{\beta}{CH_2} - \overset{\gamma}{CH_2} - \overset{\delta}{CH_3}$$

Mercury was again present in the reaction vessel. Unlike the experiments carried out with trifluoromethyl radicals, the amount of 1,1,1-trifluoro-2-iodopentane produced is very significant. Errors therefore arose from the fact that separation of this product from 1,1,1-trifluoro-3-iodopentane was very poor even under the best conditions found. The use of the Dupont curve resolver was essential in obtaining peak area measurements which were acceptable for use in kinetic studies.

The results obtained from these experiments are given in table 2/11. Using these results to plot RS_γ^α, RS_γ^β and RS_γ^δ against $10^3/T$ gave three straight lines (figure 2/8). From the slopes of these lines and their

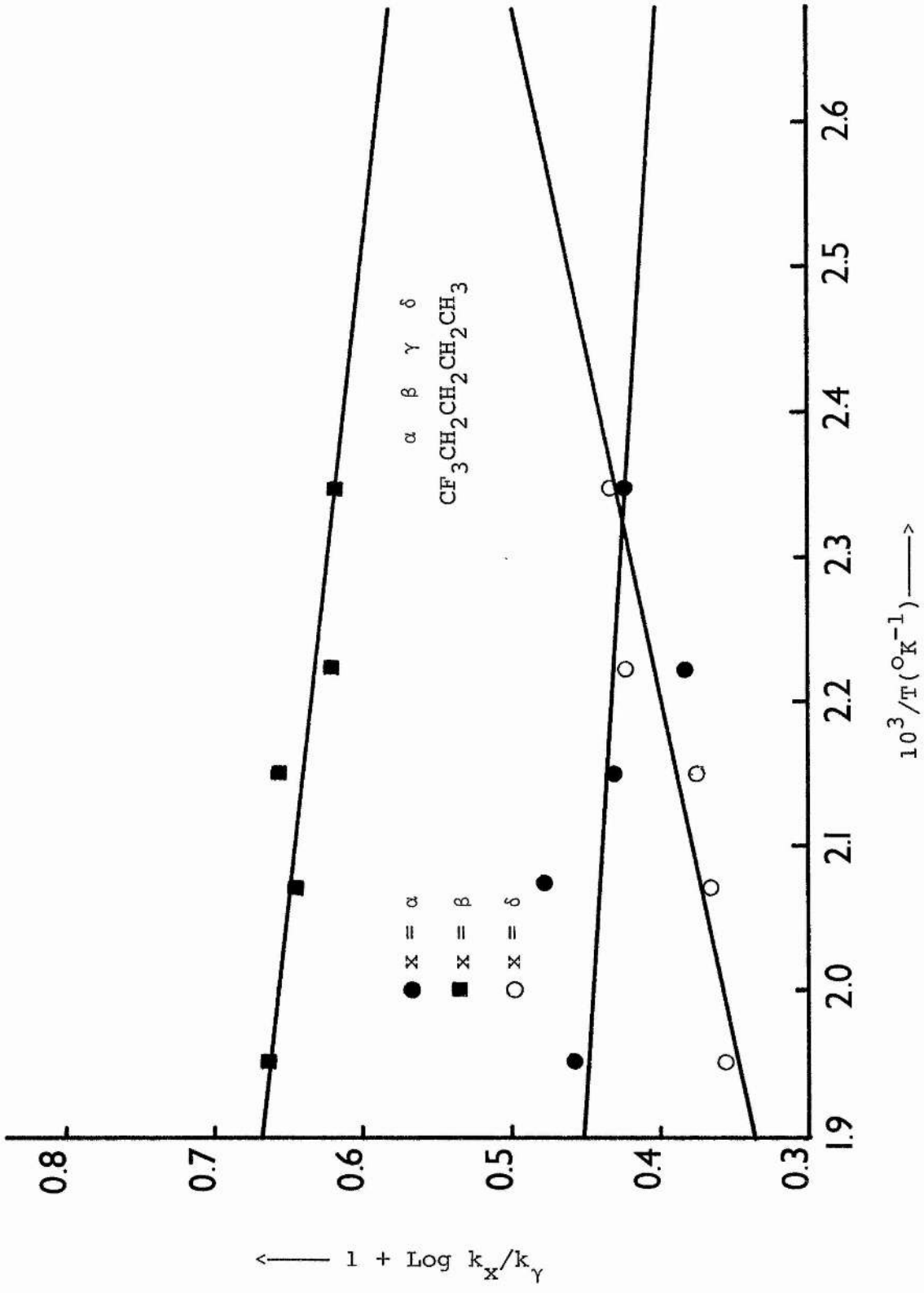


FIGURE 2/8 Methyl Radicals + 1,1,1-Trifluoropentane

intercepts with the y-axis the following results were obtained:

$E_\gamma - E_\alpha = -0.8$ kcals, $\log A_\alpha/A_\gamma = -0.181$; $E_\gamma - E_\beta = -0.6$ kcals, $\log A_\beta/A_\gamma = -0.0883$; $E_\gamma - E_\delta = +1.0$ kcals, $\log A_\delta/A_\gamma = -1.066$.

DISCUSSION

As can be seen from Table 2/12 the presence of mercury in the reaction vessel as an iodine atom scavenger has a significant effect on the results. The relative selectivities of the trifluoromethyl radicals at that particular temperature are very similar to those obtained by Whytock and workers [66].

RELATIVE SELECTIVITIES OF TRIFLUOROMETHYL RADICALS ($90^{o}C$)

CH_3 ———	CH_2 ———	CH_2 ———	CH_3	
1	7.6	7.6	1	No Mercury present
1	14.0	14.0	1	Mercury present
1	13.0	13.0	1	Whytock (ref 66)

TABLE 2/12

The Arrhenius parameters obtained however show a significant difference from those stated by Whytock whose values can be represented by the expression

$$\log k_p/k_s = -0.39 - (2633 \text{ cal mol}^{-1})/2.303\ RT$$

whereas the expression for the parameters in our experiment is

$$\log k_p/k_{su} = +0.51 - (1052 \text{ cal mol}^{-1})/2.303\ RT$$

No mention of the presence of excited iodine atoms is made by Whytock. The temperature range in Whytock's experiments was 160°C to 270°C. Evidence existed in our experiments of elimination from the butyl iodides above 190°C and this could account for the discrepancies.

The effect of substituents on hydrogen abstraction reactions of trifluoromethyl radicals is evident on reference to the relative selectivities with substituted butanes (Table 2/13).

	α	β	γ	δ
X ———	CH_2 ———	CH_2 ———	CH_2 ———	CH_3
H	1	14	14	1
F	2	2	11	1
CF_3	0.1	2	11	1

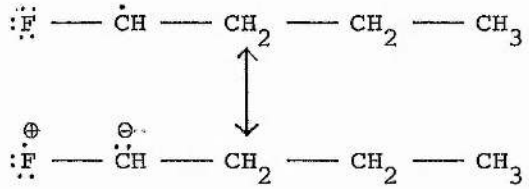
TABLE 2/13 : RELATIVE SELECTIVITIES OF TRIFLUOROMETHYL RADICALS (90°C)

A 2-fold increase in the relative selectivity in the α position exists in the case of *n*-butyl fluoride. The fluorine substituent would be expected to cause a decrease in reactivity in this position on the grounds of polarity alone. The fluorine atom reduces the electron density at the hydrogen atoms in this position and hence causes more repulsion between the hydrogen atoms and the trifluoromethyl radical.

The same reduction in electron density would be expected at the α hydrogen position in 1,1,1-trifluoropentane. Table 2/13 indicates that there is indeed a ten-fold decrease in reactivity at this position to hydrogen abstraction by trifluoromethyl radicals.

The 2-fold increase in reactivity at the α hydrogen site in *n*-butyl fluoride must therefore be due to an opposite and stronger effect than that caused by the shifting of the electron density away from the α hydrogens. This effect cannot be exerted by the trifluoromethyl group in the 1,1,1-trifluoropentane whose effect on reactivity at the different reaction sites is solely due to the electron withdrawing nature of the group.

The presence of the fluorine atom causes a decrease in D(C-H) in the α position due to the resonance stabilisation of the incipient radical. This occurs because of the presence of the lone pairs in the fluorine



Any group containing π-electrons or any atoms with non-bonded p-electrons will favour hydrogen abstraction from the carbon atom to which it is attached by resonance stabilisation of the incipient radical. In the case of *n*-butyl fluoride the activation of the α hydrogens due to the resonance stabilisation is in conflict with the deactivation by the decrease in electron density. The most dominating

influence however is clearly the resonance stabilisation of the incipient radical.

It is evident from the results considered so far that although the relative strengths of the bonds broken in these reactions is important, there are other strong influences. The hydrogen abstraction by the trifluoromethyl radicals from the α position in 1,1,1-trifluoropentane support this as there is little influence on D(C-H) by the trifluoromethyl group in the molecule whose influence is solely of a polar nature.

No resonance stabilisation occurs at the β position in *n*-butyl fluoride. From the results in Table 2/13 it is obvious that a strong deactivating influence is exerted on the hydrogen atoms attached to carbons in the β position by both fluorine and trifluoromethyl substituents. This is due to the decrease in electron density at the β reaction site due to the inductive effects of the substituents.

The results obtained are in agreement with those obtained by Coomber and Whittle [62] who studied the effect of fluorine substituents in methane and ethane to hydrogen abstraction by trifluoromethyl radicals. Whittle also found that fluorine atoms exerted a strong deactivating effect on β hydrogen reaction sites whereas the effect on α hydrogens was to lower the activation energy when only one fluorine atom was present. Whittle found that these results were compatible with previous studies of bromination reactions [81,82].

It appears from the results in Table 2/13 that the substituents have a slight deactivating effect on the γ positions. It is most likely that this difference in reactivity is entirely due to experimental error as no such effect has been found in previous studies involving other abstracting species (Tables 2/14, 2/15, 2/16).

	H —— CH_2 —— CH_2 —— CH_2 —— CH_3				ref
Cl·	1	3.8	3.8	1	33,84
t-BuO·	1	8.0	8.0	1	85,90
CF_3·	1	14.0	14.0	1	This work
Br·	1	80	80	1	84
CCl_3·	1	90	90	1	86
CH_3·	1	10	10	1	This work, 73

TABLE 2/14 : RELATIVE SELECTIVITIES OF RADICAL SPECIES REACTING WITH *n*-BUTANE

	α	β	γ	δ	
	F —— CH_2 —— CH_2 —— CH_2 —— CH_3				ref
Cl·	0.9	1.7	3.8	1	87,88,89
t-BuO·	6.8	3.3	8.0	1	90
CF_3·	2.0	2.3	11	1	This work
Br·	10	9	80	1	87
CCl_3·	7.1	-	90	1	86
CH_3·	8	10	10	1	This work, 73

TABLE 2/15 : RELATIVE SELECTIVITIES OF RADICAL SPECIES REACTING WITH *n*-BUTYL FLUORIDE

	α	β	γ	δ	
	CF_3 —— CH_2	—— CH_2	—— CH_2	—— CH_3	ref
Cl	0.03	1.7	3.8	1	87
t-BuO·	-	-	-	-	-
CF_3·	0.1	2.4	11	1	This work
Br·	1	7	80	1	87
CCl_3·	0.6	11	90	1	86
CH_3·	1.3	3	10	1	This work, 73

TABLE 2/16 : RELATIVE SELECTIVITIES OF RADICAL SPECIES REACTING WITH 1,1,1-TRIFLUOROPENTANE

The results obtained from the hydrogen abstraction reactions of methyl radicals are summarised in Table 2/17 in the form of relative selectivities. The same problems were encountered in these studies as were experienced by Tedder and Watson [79]. The

	α	β	γ	δ
	X —— CH_2	—— CH_2	—— CH_2	—— CH_3
H	1	10	10	1
F	8	10	10	1
CF_3	1.3	3	10	1

TABLE 2/17 : RELATIVE SELECTIVITIES OF METHYL RADICALS

iodine abstraction reaction

$$R^{\cdot} + CH_3I \rightleftharpoons RI + CH_3^{\cdot}$$

is reversible and for alkyl radicals the equilibrium is thought to be well over to the left. $-CF_2^{\cdot}$ is known to be very effective in iodine abstraction [14]. It is therefore reasonable to expect $CF_3CH^{\cdot}-$ and $-CFH^{\cdot}$ radicals to also be effective in iodine abstraction. Although some doubt exists over the validity of the results for hydrogen abstraction in the β and γ position (relative to the δ position) one can presume that the results for abstraction in the α position give a reasonable indication as to the reactivity at this particular site.

Assuming this to be correct the fluorine substituent in *n*-butyl fluoride has the effect of increasing the reactivity to hydrogen abstraction by methyl radicals eight-fold. This increase is to be expected on the same grounds as stated when considering the reactions of trifluoromethyl radicals. The fluorine again has the effect of reducing the electron density at the α hydrogen reaction site. In the case of trifluoromethyl radicals this had the effect of reducing the reactivity at this particular site as the trifluoromethyl radical can be considered to be strongly electrophilic in nature. Methyl radicals however are considered to be nucleophilic [83] and therefore the decrease in electron density at the α site would be expected to render the hydrogen atoms more likely to abstraction by methyl radicals.

The resonance stabilisation of the incipient radical caused by

hydrogen abstraction from the α position in *n*-butyl fluoride will increase the reactivity at this site in the same way as it did for the trifluoromethyl radicals, the weakening of D(C-H) being independent of the attacking radical. Both factors therefore increase the reactivity at the α site.

The reactivity to hydrogen atom abstraction at the α position in 1,1,1-trifluoropentane shows it to be of the same order as the δ position. The trifluoromethyl group in the molecule does not appear to be exerting any considerable effect on the reactivity at this position. As was discussed when considering trifluoromethyl radicals, the only possible effect this group could have would result from the decrease in electron density at this reaction site caused by the electron withdrawal by the trifluoromethyl group.

This result again suggests that methyl radicals do exhibit some degree of nucleophilicity. Whittle [62,81] discusses the hydrogen abstraction reactions of methyl radicals with fluoromethanes and suggests that the decrease in activation energy is going from methane to the fluoromethanes is due to a decrease in D(C-H) and that the corresponding effect with trifluoromethyl radicals is not as evident as there is a cancelling out by polar effects. This also suggests that methyl radicals have some nucleophilic character.

This nucleophilicity has also been shown in studies of hydrogen abstraction reactions from substituted toluenes, the Hammett correlations with methyl radicals giving a ρ-value marginally greater than zero [91].

The results for the relative selectivities for methyl radicals in the β and γ positions seem even more doubtful as the values are lower than the corresponding value for the trifluoromethyl radicals for abstraction from butane (Table 2/17). Trifluoromethyl radicals are about three times more reactive in abstraction reactions than are methyl radicals [50]. It would therefore be expected that methyl radicals are far more selective as to position of attack in a molecule. The value RS_p^s = 10 seems very low for methyl radicals again supporting the belief that the iodine abstraction reactions of these radicals are reversable. Iodine abstraction from the primary position is thermoneutral whereas abstraction from the secondary position is endothermic. The equilibrium would therefore be expected to lie further to the left for abstraction from the secondary position thus causing a low value for RS_p^s. The fate of the radicals cannot be explained. Any products resulting from combination, disproportionation or hydrogen abstraction reactions would probably be undetectable in the small quantities present.

The results for hydrogen atom abstraction reactions agree favourably with the results of other radical species (Tables 2/14, 2/15, 2/16). In the case of *n*-butyl fluoride the α position is activated to attack by all radicals except chlorine where little resonance stabilisation exists. The β position is also deactivated as indeed it is for the other radical species. For the reactions with 1,1,1-trifluoropentane again the results are similar to those obtained for the other radical species in both the α and β positions.

REFERENCES

1. M. Gomberg : *Chem. Ber.*, 1900, 33, 3150.

2. F. Paneth and W. Hofeditz : *Chem. Ber.*, 1929, 62B, 1335.

3. M.S. Kharasch and F.R. Mayo : *J. Am. Chem. Soc.*, 1933, 55, 2468.

4. M.S. Kharasch, H. Engelman and F.R. Mayo : *J Org. Chem.*, 1937, 2, 288.

5. D.H. Hey and W.A. Waters : *Chem. Rev.*, 1937, 21, 169.

6. F.R. Mayo and C. Walling : *Chem. Rev.*, 1940, 27, 351.

7. L. Mandelcorn and E.W.R. Steacie : *Can. J. Chem.*, 1954, 32, 474.

8. F.A. Raal and C.J. Danby : *J Chem. Soc.*, 1949, 2219.

9. L. Endrenyi and D.J. LeRoy : *J. Phys. Chem.*, 1967, 71, 1334.

10. R.J. Cvetanovic and R.S. Irwin : *J. Chem. Phys.*, 1967, 46, 1964.

11. J.M. Sangster and J.C.J. Thynne: *Int. J. Chem. Kinetics*, 1969, 1, 571.

12. L.C. Landers and D.H. Volman : *J. Am. Chem. Soc.*, 1957, 79, 2996.

13. R.K. Brinton : *J. Chem. Phys.*, 1958, 29, 781.

14. H.C. Low, J.M. Tedder and J.C. Walton : *J.C.S. Faraday I*, 1976, 72, 170

15. J.M. Tedder, J.C. Walton and K.D.R. Winton : *J.C.S. Faraday I*, 1972, 68, 1866.

16.(a) J.M. Tedder and J.C. Walton : *Trans. Faraday Soc.*, 1966, 62, 1859.

16.(b) J.A. Kerr and M. Parsonage : *Evaluated Kinetic Data on gas phase addition reactions*, Butterworths, 1972.

16.(c) J.M. Tedder, J.C. Walton and H.W. Sidebottom : *Int. J. Chem. Kinetics*, 1972, 4, 243, 249.

17. J.M. Tedder, J.C. Walton and K.D.R. Winton : *J.C.S. Faraday I*, 1972, 68, 160.

18. S. Bywater and E.W.R. Steacie : *J. Chem. Phys.*, 1951, 19, 172.

19. S. Bywater and E.W.R. Steacie : *J. Chem. Phys.*, 1951, 19, 319.

20. S. Bywater and E.W.R. Steacie : *J. Chem. Phys.*, 1951, 19, 326.

21. C.R. Masson : *J. Am. Chem. Soc.*, 1952, 74, 4731.

22. J.T. Gruver and J.G. Calvert : *J. Am. Chem. Soc.* 1956, 78, 5208.

23. J.A. Kerr and A.F. Trotman-Dickenson : *Trans. Faraday Soc.*, 1959, 55, 572.

24. J.G. Calvert and W.C. Sleppy : *J. Am. Chem. Soc.*, 1959, 81, 1544.

25. J.A. Kerr and J.G. Calvert : *J. Am. Chem. Soc.*, 1961, 83, 3391.

26. R.A. Back and S. Takamuku : *J. Am. Chem. Soc.*, 1964, 86, 2558.

27. M.C. Lin and K.J. Laidler : *Can. J. Chem.*, 1966, 44, 2927.

28. M.M. Papic and K.J. Laidler : *Can. J. Chem.*, 1971, 49, 549.

29. W.C. Smith : *U.S. Patent*, 1958, 2, 862, 029.

30. W.R. Hasek, W.C. Smith and V.A. Engelhardd : *J. Am. Chem. Soc.*, 1960, 82, 543.

31. J.A. Kerr and M.J. Parsonage : *Evaluated Kinetic Data on gas phase addition reactions*, Butterworths, 1972.

32. G. Chiltz, P. Goldfinger, G. Huybrechts, G. Martens and G. Verbeke : *Chem. Rev.*, 1963, 63, 355.

33. J. Knox and R.L. Nelson : *Trans Faraday Soc.*, 1959, 55, 937.

34. P. Goldfinger, G. Huybrechts, G. Martens, Meyers and Olbrechts : *Trans. Faraday Soc.*, 1965, 61, 1933.

35. D.H.R. Barton, A.J. Head and R.J. Williams : *J. Chem. Soc.*, 1951, 2039.

36. D.H.R. Barton and A.J. Head : *Trans. Faraday Soc.*, 1950, 46, 114.

37. E.S. Swinbourne : *Comprehensive Chemical Kinetics*, 1972, Vol. 5, Elsevier, N.Y.

38. A.L. Henne and A.M. Whaley : *J. Am. Chem. Soc.*, 1942, 64, 1157.

39. A.L. Henne and J.B. Hinkamp : *J. Am. Chem. Soc.*, 1945, 67, 1194.

40. A.L. Henne and J.B. Hinkamp : *J. Am. Chem. Soc.*, 1945, 67, 1197.

41. G.J. Martens, M. Godfroid, J. Delvaux and J. Verbeyst : *Int. J. Chem. Kinetics*, 1976, 8, 153.

42. J.M. Tedder : *Quart. Rev.*, 1960, 14, 336.

43. M.G. Evans and M. Polanyi : *Trans. Faraday Soc.*, 1938, 34, 11.

44. G.C. Fettis, J.H. Knox and A.F. Trotman-Dickenson : *J. Chem. Soc.*, 1960, 1064.

45. H.C. Andersen and E.R. Van Artsdalen : *J. Chem. Phys.*, 1944, 12, 478.

46. A.F. Trotman-Dickenson : *Quart. Rev.*, 1953, 7, 198.

47. J.A. Kerr : *Chem. Rev.*, 1966, 66, 465.

48.(a) H.B. Haas, E.T. McBee and P. Weber : *Ind. Eng. Chem.*, 1935, 27, 1190.

48.(b) H.B. Haas, E.T. McBee and P. Weber : *Ind. Eng. Chem.*, 1936, 28, 33.

49. P.G. Ashmore and J. Chanmugam : *Trans. Faraday Soc.*, 1953, 49, 254.

50. P. Gray, A.A. Herod and A. Jones : *Chem. Rev.*, 1971, 71, 247.

51. R.E. Dodd and J.W. Smith : *J. Chem. Soc.*, 1957, 1465.

52.(a) G.A. Chamberlain and E. Whittle : *Chem. Comm.*, 1971, 396.

52.(b) G.A. Chamberlain and E. Whittle : *J.C.S. Faraday I*, 1972, 68, 88.

53.(a) M.B. Fagarash, F.B. Moin, V.I. Ocheret'ko: *Kinetika i Kataliz*, 1968, 9, 920.

53.(b) M.B. Fagarash and F.B. Moin : *Kinetika i Kataliz*, 1968, 9, 1377.

54. G.O.Pritchard, H.O. Pritchard, H.I. Schiff and A.F. Trotman-Dickenson *Trans. Faraday Soc.*, 1956, 52, 849.

55. G.O. Prichard, H.O. Pritchard, H.I. Schiff and A.F. Trotman-Dickenson *Chem. and Ind.*, 1955, 564.

56.(a) A.F. Trotman-Dickenson and G.S. Milne, : *Tables of Bimolecular Gas Reactions*, National Bureau of Standards, U.S. Government Printing Office, 1967, Ref. No. NSRDS - NBS9.

56.(b) E.Ratajczak and A.F. Trotman-Dickenson : *Supplementary Tables of Bimolecular Gas Reactions*, Office of Scientific and Technical Information, 1969.

56.(c) J.A. Kerr and E. Ratajczak : *Secondary Supplementary Tables of Bimolecular Gas Reactions*, Birmingham University, 1972.

57. W.G. Alcock and E. Whittle : *Trans. Faraday Soc.*, 1965, 61, 244.

58. L.A. Oksentevich and A.N. Pravednikov : *Doklady Phys. Chem., Proc. Acad. U.S.S.R.*, 1966, 169, 541. OR *Doklady Akad. Nauk U.S.S.R.*, 1966, 169, 1130.

59. W.G. Alcock and E. Whittle : *Trans. Faraday Soc.*, 1966, 62, 134.

60. W.G. Alcock and E. Whittle : *Trans. Faraday Soc.*, 1966, 62, 664.

61. R.J. Cvetanovic, F.A. Raal and E.W.R. Steacie : *Can. J. Chem.*, 1953, 31, 171.

62. R.D. Giles, L.M. Quick and E. Whittle : *Trans. Faraday Soc.*, 1967, 63, 670.

63. S.W. Charles and E. Whittle : *Trans. Faraday Soc.*, 1966, 62, 1553.

64. E.R. Morris and J.C.J. Thynne : *Trans Faraday Soc.*, 1968, 64, 414.

65. L.M. Quick and E. Whittle : *Trans. Faraday Soc.*, 1971, 67, 1727.

66. M.H. Arican, E. Potter and D.A. Whytock : *J.C.S. Faraday I*, 1973, 69, 1811.

67. A.F. Trotman-Dickenson, *"Gas Kinetics"*, Butterworths, London, 1958,

68. A. Shepp : *J. Chem. Phys.*, 1956, 24, 939.

69. W.M. Jackson, J.R. McNesby and B. deB. Derwent : *J. Chem. Phys.*, 1962, 37, 1610.

70. F.A. Raal and E.W.R. Steacie : *J. Chem. Phys.*, 1952, 20, 578.

71. G.O. Pritchard, J.T. Bryant and R.L. Thommarson : *J. Phys. Chem.*, 1965, 69, 664.

72. G.O. Pritchard and R.L. Thommarson : *J. Phys. Chem.*, 1964, 68, 568.

73.(a) J.M. Tedder and R.A. Watson : *J. Chem. Soc. (B)*, 1966, 1069.

73.(b) R.A. Watson : *Ph.D. Thesis (Sheffield)* 1965.

74. F.O. Rice and T.A. Vandersliee: *J. Am. Chem. Soc.*, 1958, 80, 292.

75. F.W. Hoffmann : *J. Am. Chem. Soc.*, 1948, 70, 2596.

76. A.J. Parker : *Adv. Org. Chem.*, 1955, 5, 1.

77. P.S. Fredricks : *Ph.D. Thesis* (Sheffield) 1960.

78. H.C. Low : *Ph.D. Thesis*, (St. Andrews) to be written.

79. D. Goodeve and C.F. Porret, *Proc. Roy. Soc.*, 1938, A165, 31.

80. G. Herzberg and G. Scheibe : *Z. Phys. Chem (Leipzig)*, 1930, 7, 390.

81. J.W. Coomber and E. Whittle : *Trans. Faraday Soc.*, 1966, 62, 1553.

82. A.M. Tarr, J.W. Coomber and E. Whittle : *Trans. Faraday Soc.*, 1965, 61, 1182.

83. J.M. Tedder and J.C. Walton : *Acc. Chem. Res.*, 1976, 9, 183.

84. P.C. Anson, P.S. Fredricks and J.M. Tedder : *J. Chem. Soc.*, 1959, 918.

85. J.L. Brokenshire, A. Nechvatal and J.M. Tedder : *Trans. Faraday Soc.*, 1970, 66, 2029.

86. J.M. Tedder and R. Watson : *Trans. Faraday Soc.*, 1968, 64, 1304.

87. I. Galiba, J.M. Tedder and R. Watson : *J. Chem. Soc.*, 1964, 1321.

88. P.S. Fredricks and J.M. Tedder : *J. Chem. Soc.*, 1960, 144.

89. P.S. Fredricks and J.M. Tedder : *Chem. Ind.*, 1959, 480.

90. I.K. Stoddart, A. Nechvatal and J.M. Tedder : *J. Chem. Soc.*, 1974, 473.

91. W.A. Pryor, U. Tonellato, D.L. Fuller and S. Jumonville : *J. Org. Chem.*, 1969, 34, 2018.